MODELING BIOTIC AND ABIOTIC DECAY OF TRICHLOROETHYLENE (TCE) USING THE REACTIVE MULTI-SPECIES TRANSPORT IN 3-DIMENSIONAL GROUNDWATER AQUIFERS (RT3D) CODE

BY

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THESIS

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Abstract

Removal of dense non aqueous phase liquids, DNAPLS, such as trichloroethylene, TCE, is vital to improving the health of groundwater systems. TCE contamination of groundwater systems is of significant concern and its removal a significant challenge. One of the main causes of delays in cleanup of a TCE contaminated site results from back diffusion. Back diffusion occurs when the TCE mass in the high permeability zones, HPZ, is removed and the TCE trapped in the low permeability zones, LPZ, of the heterogeneous aquifer diffuses out due to concentration gradient reversal and re-contaminates the site. Several studies have indicated that TCE can be transformed into less harmful products of interest via biotic and abiotic processes. These processes are slow but may potentially have an impact since TCE can spend long time periods in LPZs as the mass transport is mainly by diffusion. The biotic process uses an organic solute such as lactate as an electron donor and the halogenated compounds as electron acceptors to biologically transform TCE into dichloroethylene (DCE), vinyl chloride (VC), and ethene. Additionally, the abiotic process transforms TCE into acetylene using reduced iron species as an electron donor. Furthermore, oxidized iron produced from the abiotic process can be converted back into the reduced form by iron reducing bacteria using lactate as a donor. These feedbacks between the biotic and abiotic processes can thus extend the transformation of TCE into acetylene. Reactive transport modeling is a useful tool to study these feedbacks. This thesis successfully develops a clear quantitative model of these decay processes using the Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers (RT3D) code. RT3D is part of the MODFLOW family of codes that is commonly used in engineering practice. In addition, this thesis explores the mitigation of the effects of back diffusion by implementing these decay processes in a 2-Dimensional flow cell model. The flow cell is built using Aquaveo Groundwater

Modeling System, GMS, while the 2-D flow simulation is performed using USGS MODFLOW, United State Geological Survey Modular Groundwater Flow Model, and the transport simulation is done using RT3D. Lastly, this thesis explains the procedures used in implementing the RT3D user-defined dynamic link library option, which is necessary when user-defined reactions are required.

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Table of Contents

Chapter 1. Introduction

Dense non-aqueous phase liquids, DNAPLs, such as trichloroethylene (TCE) and its daughter products, dichloroethylene (DCE) and vinyl chloride (VC), are a major form of groundwater contamination. In a study conducted of 315 New Jersey wells, approximately 20% were found to be contaminated with TCE; similar results were found in Nebraska where roughly 15% of the sampled wells were found to be contaminated with TCE (Russell et al., 1992). TCE is typically used as a universal degreasing agent, leading to its higher prevalence in more industrialized areas. Additionally, TCE and its daughter products pose significant health risks. TCE has been shown to cause adverse health effects if processed by the human liver, while VC is a known carcinogen (Russell et al., 1992). Due to its significant prevalence and its impact on human health it is imperative to remove TCE and its harmful variants from groundwater supply.

It is widely known that the most difficult cleanup sites consist of those containing DNAPLs along with highly heterogeneous geology (Wiedemeier et al., 1999; Macdonald and Kavanugh, 1994). This is because as the DNAPL source leaks into the subsurface, the DNAPL can penetrate vertically below the water table due to its high density, resulting in large vertically and horizontally extensive plumes of dissolved contamination. (Wiedemeier et al., 1999). In addition, in a heterogeneous environment the DNAPL initially contaminates the high permeability zones, HPZ, such as sand and over a long period diffuses into the low permeability zones, LPZ, such as rock and clay. Once the DNAPL mass in the HPZ is removed either through natural attenuation, source removal, or active remediation methods such as pump and treat, the DNAPL located in the LPZ diffuses out, as the concentration gradient reverses, and the contaminant is reintroduced to the subsurface environment. This reintroduction of contaminant is known as back diffusion. Back diffusion can often result in prolonging of remediation efforts.

TCE, in particular, poses challenges to site remediation due to TCE's low maximum contaminant level (MCL), MCL for TCE is 5ppb, and 2ppb for VC respectively, by increasing the treatment efforts needed to reach the MCL (Wiedemeier et al., 1999).

Several studies have indicated the adverse effects of back diffusion in site remediation. A study conducted by Chapman *et al*, 2012, referenced in Figures 1.1 and 1.2, mimicked field conditions using a 2-D laboratory flow cell experiment. Figure 1.1, shows the configuration of LPZs embedded into a background of high permeability sand. Figure 1.2 shows the breakthrough curve of tracer measured in influent and effluent. The study showed that tracer loading and diffusion into the LPZ required only 22 days to reach peak contamination level of 90 mg/L, but it then took another 100 days for all tracer trapped in the LPZ to be flushed out and to return from the previous high to its initial condition (Chapman et al., 2012). This study effectively shows the resulting delay caused by back diffusion which leads to significant increases in cost and time taken during remediation efforts.

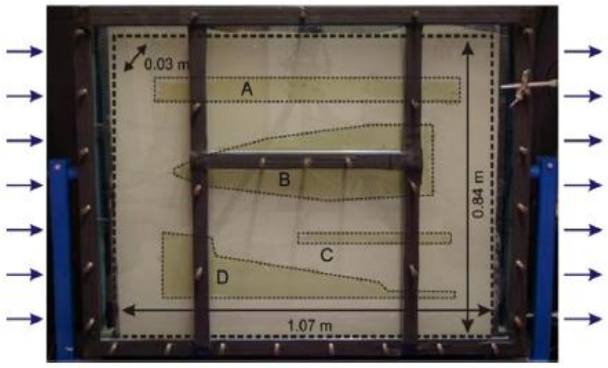

Figure 1.1. Flow cell referenced in the study conducted by Chapman et al. The darker shapes are locations of the LPZ (Chapman et al., 2012).

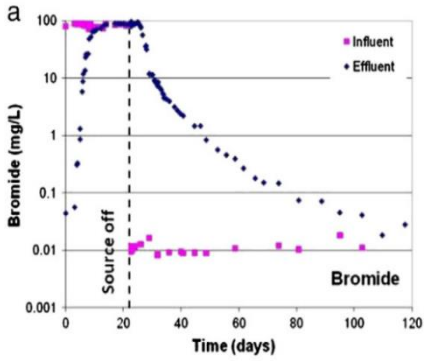

Figure 1.2. Shows the difficulties which arise in remediation because of back diffusion process (Chapman et al., 2012).

Another example of the impact of back diffusion is a TCE impacted field site in Cocoa, FL (Parker el al., 2008). At this site TCE was released from mid- to-late 1960s until 1977, but due to back diffusion the site remained contaminated even after source removal and remedial

efforts. A core sample from the site, shown in Figure 1.3, indicated that a significant proportion of the mass was trapped in the LPZ, thus suggesting back diffusion as the primary cause in the delayed cleanup efforts. Additionally, in Figure 1.4 numerical simulations conducted using field conditions with multiple LPZs show that even 50 years after the source is removed significant amounts of TCE will remain due to back diffusion (Parker el al., 2008). Thus, understanding back diffusion in LPZs is important to efficiently implement a site remediation effort and to reduce the uncertainty in the time scales needed for cleanup.

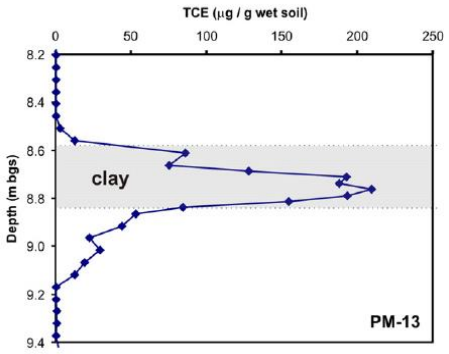

Figure 1.3. Indicates that a significant proportion of TCE is trapped in the LPZ, causing delayed cleanup efforts (Parker el al., 2008).

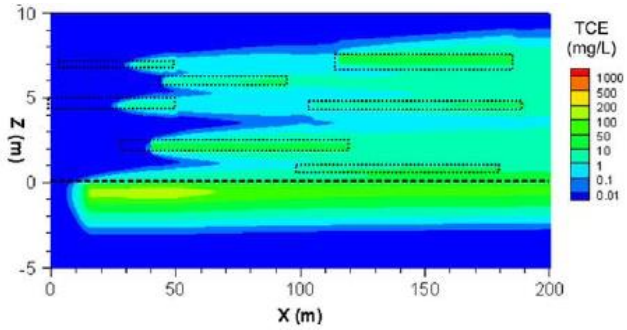

Figure 1.4. Results of numerical simulation. Shows that TCE remains present 50 years after source removal, as a result of back diffusion (Parker el al., 2008).

TCE can be transformed through biotic and abiotic processes. Several studies have indicated that chlorinated ethenes can act as electron acceptors and can be reduced biologically in the presence of an electron donor under anaerobic conditions (Bradley, 2003). This process is known as reductive dechlorination. Reductive dechlorination converts TCE to DCE to VC to ethene by sequentially removing a Cl- ion in the presence of an electron donor. Specifically, TCE has been converted biologically to ethene using lactate as an electron donor (Kerr et al., 1994). Additionally, LPZs have been shown to promote increased microbial biomass, by potentially providing protection from predation (Heijnen and van Veen, 1991). This can increase

the amount of natively present dechlorinating bacteria in the LPZ and hence the decay of TCE, as lactate or another electron donor diffuses into the LPZ. Another mechanism for TCE decay is a combination of abiotic and biotic processes. Several studies have shown that Fe(II) in minerals in the LPZ can react abiotically to sequentially degrade TCE and its variants (Elsner, 2002; Ferrey et al., 2004; Lee and Batchelor, 2002a, 2002b; O'Loughlin and Burris, 2004; Weerasooriya and Dharmasena, 2001). In these reactions, Fe(II) is the electron donor and is hence transformed into Fe(III) in the presence of TCE, the electron acceptor, to convert TCE into acetylene; see details in Chapter 3. Fe(III) can be reduced biologically to Fe(II) in the presence of iron-reducing bacteria, provided that there is an available electron donor. Such abiotic reactions have been shown to extensively mitigate the effects of back diffusion in natural rock matrices (Schaefer et al., 2013). Despite these studies a clear quantitative model is needed to understand the aforementioned TCE decay reactions within the LPZ and at the HPZ-LPZ interface, and its resulting effects on back diffusion. This model will also highlight the competitive and interactive parts of coupling biotic and abiotic reactions.

This thesis aims to model biotic and abiotic reactions that impact fate and transport of TCE in and around the boundaries of the LPZ. Specifically, this thesis will implement biotic interaction consisting of TCE/Lactate and an abiotic/biotic interaction consisting of TCE/Fe(II)/Lactate using the RT3D numerical code. RT3D is part of the MODFLOW family of codes and is widely used in engineering practice (Alvarez and Illman, 2006). RT3D includes some "pre-packaged" reaction modules, including sequential first-order transformation of TCE to DC to VC to ethene. However, the pre-packaged modules do not explicitly account for the electron donor (e.g. lactate) and do not consider abiotic reactions. Therefore, a major goal of the thesis is to use the user-defined reaction capability of RT3D to implement abiotic reactions.

The thesis is organized as follows. Chapter 2 presents the model for biotic transformation of TCE through sequential dechlorination reactions. Although these reactions have already been used extensively in the literature and are provided as a pre-packaged reaction module in RT3D, we add the possibility that the reaction rate can be limited by the concentration of the electron donor (assumed to be lactate). Chapter 2 presents testing and validation of the reaction model, and models transport in an experimental flow cell with a single HPZ and LPZ designed and built by collaborators at University of Texas Austin. Chapter 3 presents the abiotic reactions and couples them with the biotic reactions. The coupled system is tested and then used for the flow cell simulations. Chapter 4 provides conclusions followed by the references. Appendix A provides the compiling instructions for compiling the RT3D user defined reactions. Appendix B presents the instructions for creating the flow cell, used in Chapters 2 and 3, in Aqauveo GMS, Groundwater Modeling System, version 10.2. Lastly, Appendix C provides instructions on testing the RT3D user defined subroutine in batch mode.

Chapter 2. Model Development for Biological Transformation of TCE

2.1 Background of RT3D

RT3D, Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers, is a reactive transport code that is designed to solve the advection-dispersion-reaction equation for multiple species subject to coupled reactions (Clement, 1997). It is a more generalized version of the MT3DMS, Modular 3-Dimensional Multispecies Transport, code. The primary advantage of RT3D is that the code provides the user with the option to add user defined kinetic reactions. Additionally, RT3D uses the implicit method to solve its reaction package (Clement, 1997). Beside these differences, RT3D primarily relies on the MT3DMS' advection, dispersion and source/sinks packages to account for fate and transport of the contaminant (Clement, 1997, 2002). Furthermore, RT3D, utilizes reaction operator splitting for computation (Clement, 1997; Zheng et al., 1999). Lastly, both RT3D and MT3DMS rely on MODFLOW, Modular Groundwater Flow Model, to solve for the flow field which is subsequently used by RT3D (Clement, 1997; Harbaugh et al.,2000; Zheng et al., 1999).

MODFLOW was initially documented by McDonald and Harbaugh in 1984 and was subsequently developed at USGS, United State Geologic Survey (Harbaugh et al., 2000). The first major revision of MODFLOW occurred in 1988, called MODFLOW-88 (Harbaugh et al., 2000). MT3D was first developed by Zheng *et al.* in 1990 at S.S. Papadopulos & Associates, Inc. with partial support from the United States Environmental Protection Agency (Bedekar et al., 2016). A second version of MT3D called MT3DMS was developed by Zheng *et al.* in 1999 for the United States Army Corps of Engineers (Zheng et al., 1999). RT3D was then built in addition to MT3D by T.P. Clement at the Battelle Pacific Northwest National Laboratory, allowing for the addition of more flexible kinetic rate laws (Clement, 1997, 2002). A brief overview of the

advection-dispersion-reaction equation and its relation to the groundwater flow equation is provided below.

Contaminant transport is governed by four processes: advection, diffusion, mechanical dispersion and reactions. Advection is controlled by the flow velocity of the fluid carrying the contaminant whereas diffusion refers to transport due to change in concentration gradient and mechanical dispersion results from the deviations in the microscale velocities relative to the average velocity. Despite the differences in dispersion and diffusion, both are modeled as a Fickian process. The combination of mechanical dispersion and diffusion is referred to as hydrodynamic dispersion or simply dispersion. Lastly, the reaction term contains the chemistry. The generalized advection-dispersion-reaction equation combines these four processes into the following partial differential equation (Zheng et al., 1999) :

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\left(\frac{\partial C}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(\theta v_i C) + q_s C_s + \Sigma R_n \qquad (2.1)$$

θ = Porosity [unitless]

q_s = Volumetric flow rate per unit volume in source/sink [T^{-1}]

t = Time [T]

C = Dissolved concentration [ML^{-3}]

C_s = Concentration of source/sink [ML^{-3}]

D_{ij} = Hydrodynamic dispersion [L^2T^{-1}]

ΣR_n =Chemical reaction term [$ML^{-3}T^{-1}$]

v_i = Seepage or linear pore water velocity [LT^{-1}]

x_i = Distance along Cartesian coordinate axis [L]

The advection-dispersion-reaction equation can be rewritten by applying the chain rule to transient partial derivative and assuming that the local equilibrium assumption can be applied to the various sorption process (Zheng et al., 1999), Equation 2.1 becomes:

$$R\theta\frac{\partial(C)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\left(\frac{\partial C}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(\theta v_i C) + q_s C_s - q_s' C + \Sigma R_n \qquad (2.2)$$

$R = 1 + \frac{p_b}{\theta}\frac{\partial \bar{C}}{\partial C}$

R = Retardation factor [unitless]

p_b = Bulk density [ML^{-3}]

$\bar{C}$ = Sorbed Concentration [MM^{-1}]

$q_s' = \frac{\partial \theta}{\partial t}$

q_s' = Transient groundwater storage [T^{-1}]

Linkage between the groundwater flow field, created by MODFLOW, and advection-dispersion-reaction equation, used by RT3D, occurs via Darcy's law and the groundwater flow equation. The groundwater flow equation is used by MODFLOW to solve for the head and is as follows:

$$S_s\left(\frac{\partial h}{\partial t}\right) = \frac{\partial}{\partial x_i}\left(K_i\left(\frac{\partial h}{\partial x_i}\right)\right) + q_s \qquad (2.3)$$

S_s =Specific storage of the aquifer [L^{-1}]

h = Hydraulic head [L]

q_s = Fluid source/sink term

K_i = Hydraulic conductivity tensor [LT^{-1}]

Darcy's law is used to solve for flow velocities, given the heads from the groundwater flow equation and is as follows:

$$v_i = -\left(\frac{K_i}{\theta}\right)\left(\frac{\partial h}{\partial x_i}\right) \qquad (2.4)$$

This thesis will use RT3D, specifically it's user defined capabilities, to model the biotic and abiotic transformations of TCE. The next section will describe the biologically mediated reduction of TCE using lactate as an electron donor. Abiotic processes will be discussed in Chapter 3.

2.2 Lactate/TCE Chemistry

Reductive dechlorination is typically modeled using chemical kinetics, represented in the form of rate laws. A rate law for a generic reaction A+ B -> products is of the form:

$$\frac{d[A]}{dt} = -k_a[A]^m[B]^n \quad (2.5)$$

$[A]$ = concentration of chemical A

$[B]$ = concentration of chemical B

k_a = Experimentally determined rate constant

m, n = Experimentally determined reaction exponents; m and n are assumed to be 1 for a second order rate law.

Other simpler rate laws are also used in practice, such as first or zero order kinetics.

It is well known that chlorinated ethenes, such as TCE, can serve as electron acceptors for anaerobic biological reaction. Since one chlorine atom is removed, this process is known as reductive dechlorination (Alvarez and Illman, 2006; Bradley, 2003). In bioremediation projects, an aqueous electron donor can be input to simulate dechlorination (Alvarez and Illman, 2006). This chapter will model reductive dechlorination using lactate as an electron donor. The overall reduction-oxidation (redox) chemistry modeled in this chapter is as follows:

$$2\ C_2HCl_3 + CH_3CHOHCOO^- + H_2O \rightarrow 2\ C_2H_2Cl_2 + CH_3COO^- + CO_2 + 2\ H^+ + 2\ Cl^- \quad (R2.1)$$

$$2\ C_2H_2Cl_2 + CH_3CHOHCOO^- + H_2O \rightarrow 2\ C_2H_3Cl + CH_3COO^- + CO_2 + 2\ H^+ + 2\ Cl^- \quad (R2.2)$$

$$2\ C_2H_3Cl + CH_3CHOHCOO^- + H_2O \qquad \text{(R2.3)}$$

$$\rightarrow 2\ C_2H_4 + CH_3COO^- + \ CO_2 + 2\ H^+ + 2\ Cl^-$$

Table 2.1. Chemical formula and the corresponding name of compounds used in the biotic reaction of TCE.

Chemical Formula	Name
C_2HCl_3	Trichloroethylene (TCE)
$C_2H_2Cl_2$	Dichloroethylene (DCE)
C_2H_3Cl	Vinyl Chloride (VC)
C_2H_4	Ethene
$CH_3CHOHCOO^-$	Lactate
CH_3COO^-	Acetate

Lastly, the above stated redox reactions will be modeled assuming second order rate laws. All of the following rate laws require the chemical concentrations to be in moles/liter.

$$\frac{d[TCE]}{dt} = \ -k_{tce}[TCE] * [Lactate] \qquad (2.6)$$

$$\frac{d[DCE]}{dt} = \ -k_{dce}[DCE] * [Lactate] + k_{tce}[TCE] * [Lactate] \qquad (2.7)$$

$$\frac{d[VC]}{dt} = \ -k_{vc}[VC] * [Lactate] + k_{dce}[DCE] * [Lactate] \qquad (2.8)$$

$$\frac{d[Ethene]}{dt} = \ k_{vc}[VC] * [Lactate] \qquad (2.9)$$

$$\frac{d[Lactate]}{dt} = \ -\left(\frac{1}{2}\right) * k_{tce} * [TCE] * [Lactate] \ -\left(\frac{1}{2}\right) * k_{dce} * [DCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{vc} * [VC] * [Lactate] \qquad (2.10)$$

The fate and transport of the above stated Lactate/TCE system can be simulated by solving the following partial differential equations which are based on mass balance:

$$R_{TCE}\frac{\partial(\theta[TCE])}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\left(\frac{\partial[TCE]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(\theta v_i[TCE]) + q_s[\mathrm{TCE}]_s - k_{tce}[TCE] * [Lactate] \quad (2.11)$$

$$R_{DCE}\frac{\partial(\theta[DCE])}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\left(\frac{\partial[DCE]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(\theta v_i[DCE]) + q_s[\mathrm{DCE}]_s - k_{dce}[DCE] * [Lactate] + k_{tce}[TCE] * [Lactate] \quad (2.12)$$

$$R_{VC}\frac{\partial(\theta[VC])}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\left(\frac{\partial[VC]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(\theta v_i[VC]) + q_s[\mathrm{VC}]_s - k_{vc}[VC] * [Lactate] + k_{dce}[DCE] * [Lactate] \quad (2.13)$$

$$R_{Ethene}\frac{\partial(\theta[Ethene])}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\left(\frac{\partial[Ethene]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(\theta v_i[Ethene]) + q_s[\mathrm{Ethene}]_s + k_{vc}[VC] * [Lactate] \quad (2.14)$$

$$R_{Lactate}\frac{\partial(\theta[Lactate])}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\left(\frac{\partial[Lactate]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(\theta v_i[Lactate]) + q_s[\mathrm{Lactate}]_s - \left(\frac{1}{2}\right) * k_{tce} * [TCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{dce} * [DCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{vc} * [VC] * [Lactate] \quad (2.15)$$

2.3 Creating a RT3D User Defined Package

Partial differential equations, Equations 2.11 through 2.15, discussed in Section 2.2 will be solved using RT3D. Using the operator splitting strategy, the reaction kinetics can be split into the set of following ordinary differential equations (Valocchi and Malmstead, 1992).

$$\frac{d[TCE]}{dt} = \frac{-k_{tce}[TCE] * [Lactate]}{R_{TCE}} \tag{2.16}$$

$$\frac{d[DCE]}{dt} = \frac{-k_{dce}[DCE] * [Lactate] + k_{tce}[TCE] * [Lactate]}{R_{DCE}} \tag{2.17}$$

$$\frac{d[VC]}{dt} = \frac{-k_{vc}[VC] * [Lactate] + k_{dce}[DCE] * [Lactate]}{R_{VC}} \tag{2.18}$$

$$\frac{d[Ethene]}{dt} = \frac{k_{vc}[VC] * [Lactate]}{R_{Ethene}} \tag{2.19}$$

$$\frac{d[Lactate]}{dt} = \frac{-\left(\frac{1}{2}\right) * k_{tce} * [TCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{dce} * [DCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{vc} * [VC] * [Lactate]}{R_{Lactate}} \tag{2.20}$$

RT3D allows the user to specify an arbitrary number of dissolved species that are modeled by the advection-dispersion-reaction equation. Immobile species can also be defined. Users can write their own subroutines to define the kinetic rate laws; the subroutine is written in Fortran 90, although some portions use the format for Fortran 77, namely the fact that line continuation occurs in column 6 with an ampersand symbol and that comments can start with the letter c. Despite this, the main RT3D program is written in Fortran 90 (Pacific Northwest National Lab, 2012). The subroutines can have reaction parameters which are spatially constant or vary within each grid block. This section will describe the RT3D user defined reaction subroutine used to solve the above defined set of differential equations, Equations 2.16 through 2.20. The code used to create the user defined package is shown below in Table 2.2.

Table 2.2. RT3D user defined subroutine describing Equations 2.16 through 2.20.

```
c
c
c
      SUBROUTINE Rxns(ncomp,nvrxndata,j,i,k,y,dydt,
     &poros,rhob,reta,rc,nlay,nrow,ncol,vrc)
C*Block 1:*********************************************************************
c List of calling arguments
c ncomp - Total number of components
c nvrxndata - Total number of variable reaction parameters to be input via RCT file
c J, I, K - node location (used if reaction parameters are spatially variable)
c y - Concentration value of all component at the node [array variable y(ncomp)]
c dydt - Computed RHS of your differential equation [array variable dydt(ncomp)]
c poros - porosity of the node
c reta - Retardation factor [ignore dummy reta values of immobile species]
c rhob - bulk density of the node
c rc - Stores spatially constant reaction parameters (can dimension upto 100 values)
c nlay, nrow, ncol - Grid size (used only for dimensioning purposes)
c vrc - Array variable that stores spatially variable reaction parameters

C*End of Block 1***************************************************************

C*Block 2:*********************************************************************
C* *Please do not modify this standard interface block*
      !MS$ATTRIBUTES DLLEXPORT :: rxns
      IMPLICIT NONE
      INTEGER ncol,nrow,nlay
      INTEGER ncomp,nvrxndata,j,i,k
      INTEGER, SAVE :: First_time=1
      DOUBLE PRECISION y,dydt,poros,rhob,reta
      DOUBLE PRECISION rc,vrc
      DIMENSION y(ncomp),dydt(ncomp),rc(100)
      DIMENSION vrc(ncol,nrow,nlay,nvrxndata),reta(ncomp)
C*End of block 2***************************************************************

C*Block 3:*********************************************************************
c *Declare your problem-specific new variables here*
      DOUBLE PRECISION tce,dce,vc,ethene,lactate,ktce,kdce,kvc
C*End of block 3***************************************************************

C*Block 4:*********************************************************************
C*Initialize reaction parameters here, if required*
       IF (First_time .EQ. 1) THEN
          First_time = 0 !reset First_time to skip this block later
       END IF
```

Table 2.2 (cont.). RT3D user defined subroutine describing Equations 2.16 through 2.20.

```
C*End of block 4************************************************************

C*Block 5:*****************************************************************
C*Assign or compute the values of new variables, if required*
      tce = y(1)
      dce = y(2)
      vc = y(3)
      ethene = y(4)
      lactate = y(5)
      !ktce = rc(1) ! Use in batch mode
      !kdce = rc(2)
      !kvc = rc(3)
      ktce = vrc(j,i,k,1) ! Use in GMS model to spatially vary constants
      kdce = vrc(j,i,k,2)
      kvc = vrc(j,i,k,3)
C*End of block 5************************************************************

C*Block 6:*****************************************************************
C*Differential Reaction Equations*
      dydt(1) = (- ktce*tce*(lactate))/reta(1)
      dydt(2) = (- kdce*dce*(lactate) + ktce*tce*(lactate))/reta(2)
      dydt(3) = (- kvc*vc*(lactate) + kdce*dce*(lactate))/reta(3)
      dydt(4) = (kvc*vc*(lactate))/reta(4)
      dydt(5) = (-0.5*ktce*tce*(lactate) -0.5*kdce*dce*(lactate)
     &          -0.5*kvc*vc*(lactate))/reta(5)
C*End of block 6************************************************************
      RETURN
      END
```

Block 1 of the user defined code explains the data structures and names of the calling arguments passed in the RT3D main program. The comments in the block 1 explain the arguments used later in the subroutine. Block 2 is the interface block and defines the type of calling arguments used to reference the RT3D main program. Block 3 initializes the names of the user defined variables and rate constants. Block 4 should remain as is, and was previously used to assign the reaction rate constants. The usage of this block was avoided because of compiling issues, discussed in Appendix A, and instead the reaction parameters are in block 5. Block 5 is

used to assign the reaction parameters and variables to the calling arguments. It is used to transfer names of certain variables used in the RT3D main program into meaningful names for the user defined reaction subroutine, for e.g. the array y(1) will correspond to computed concentration values related to TCE and similarly y(2) will correspond to DCE etc. Block 5 is also used to define the reaction rate constants; the vector rc (*) in this block is used to define spatially constant parameters, whereas the array vrc(i,j,j,*) is used to allow for spatially variable rate constants at each grid cell (i,j,k). It is important to note that the vrc array is only accessible when modeling the entire domain and is not accessible in batch reaction mode. For the batch mode, only rc is used to define the rate constants.

RT3D allows the user to run either in batch mode or in a full simulation. Batch mode only computes the reaction terms of the advection-dispersion-reaction equation, Equation 2.1. The user can use batch mode to debug reaction rate laws, test out for reasonable rate constants and lastly select appropriate tolerance values (Clement, 1997). A more detailed discussion of batch mode is provided in Section 2.4. In addition, the full simulation of RT3D can be performed using several popular graphical user interfaces, including Groundwater Vistas and Groundwater Modeling System, GMS (Scientific Software Group; Aquaveo). This thesis will use GMS version 10.2 to model the entire domain; details are discussed in Section 2.6. Lastly, block 6 contains the user defined rate laws; the reta(species_number) calling argument contains the retardation coefficients for a given species. It is also important to note that the code must be compiled using Intel Visual Fortran, instructions for compiling are provided in Appendix A.

Several errors occurred when calling the RT3D executable alongside the user defined dynamic link library, dll. The procedure of calling the RT3D executable is as follows: write the user defined subroutine (1), compile the subroutine into a dll (2), place the dll in the folder

containing the RT3D executable (3), and lastly run the RT3D executable. The errors occurred when the compiled dll did not properly communicate with the RT3D executable. This was because the RT3D code was compiled in the later 1990's and early 2000's possibly using Compaq Visual Fortran and the dll was compiled using Intel Visual Fortran, successor to Compaq Visual Fortran. A brief discussion of the errors and solutions to such errors is provided in Appendix A.

2.4 Verification of TCE/Lactate Model

Once the subroutine discussed in Section 2.3 is compiled into a dll, the model can be tested in batch mode using the rt3dbat1.exe provided by Groundwater Modeling Systems, GMS, software. The batch utility numerically solves the rate laws explained in Section 2.3, Equations 2.16 through 2.20. Additionally, the batch utility assumes a retardation coefficient of 1. Furthermore, in order to verify the model, the model results can be compared to analytical solutions, if they are available, or to an independent numerical solution. In this section, the batch RT3D results are compared to a numerical solution using the explicit method. Another method is to verify the mass balance.

The batch utility is run by placing rt3dbat1.exe in the folder where the compiled rxns.dll file is located. Then the batch utility can be called by running rt3dbat1.exe and answering the questions prompted by the utility. For the cases explored in this section, ncomp, i.e. number of species, will be 5, no_of_timesteps will be 10 and delt is 1. The first question of the batch utility asks for the number of mobile species, the number of timesteps needed to model and lastly the length of each time step. Once these values are entered the next question will ask for the initial values of each of the mobile species, in the same order as Block 5 of the subroutine. The next question will address the tolerance of the solution, type n to keep the default values, described in

the RT3D manual. The next question asks for the number of rate constant used in dll, enter 3. The last question will require the user to enter the values for each of the rate constants. The values used for ktce, kdce, and kvc are 0.005, 0.003, and 0.001, respectively. It is important to note that RT3D doesn't require units as long the units are consistent but in this case the units for all concentrations are moles/liter or mol/l and for rate constants the units are Liter/(moles*day), leaving time to be in days. Step by step instructions for running the batch mode for a scenario 1 are provided in Appendix C.

We will test three scenarios with different initial values in order to verify the model, listed below. The three tested scenarios are:

1. A value of 100 is entered for TCE leaving others as 0. This will confirm that no DCE, VC and ethene are formed without lactate. Additionally, this run will also confirm that TCE remains at 100, hence verifying mass balance.
2. A value of 100 will be entered for lactate leaving others 0. Similar to run 1, no DCE, VC and ethene should form and the lactate concentration will remain 100, satisfying mass balance.
3. A value of 100 will be entered for TCE and lactate, respectively. In this case, DCE, VC and ethene should form and the sum total of TCE, DCE, VC and ethene should be 10 for any given timestep, thus satisfying mass balance. A secondary verification will be performed using the explicit method to compare the results from the batch utility.

The results from batch mode accurately verified the user defined subroutine created in this section. Table 2.3 accurately shows the results for scenario 1, where no DCE, VC, and ethene formed due to a lack of lactate and the input concentration of TCE remained constant throughout the simulation period, thus meeting the mass balance. Table 2.4, for scenario 2, also

showed no formation of DCE, VC, and ethene while lactate concentration held firm, satisfying mass balance. Lastly for scenario 3, Table 2.5 confirmed that DCE, VC and ethene formed as TCE and lactate continued to decay. Mass balance was also met, shown in Table 2.6, as the sum concentration of TCE, DCE, VC and ethene totaled the initial input concentration of TCE.

Table 2.3. Batch mode results from scenario 1.

Time	TCE	DCE	VC	Ethene	Lactate
0.00000E+00	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.10000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.20000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.30000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.40000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.50000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.60000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.70000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.80000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.90000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.10000E+02	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00

Table 2.4. Batch mode results from scenario 2.

Time	TCE	DCE	VC	Ethene	Lactate
0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.10000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.20000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.30000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.40000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.50000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.60000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.70000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.80000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.90000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.10000E+02	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03

Table 2.5. Batch mode results from scenario 3.

Time	TCE	DCE	VC	Ethene	Lactate
0.00000E+00	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+03
0.10000E+01	0.64048E+02	0.31236E+02	0.45702E+01	0.14517E+00	0.79594E+02
0.20000E+01	0.44648E+02	0.42486E+02	0.12129E+02	0.73644E+00	0.65523E+02
0.30000E+01	0.33055E+02	0.46034E+02	0.19233E+02	0.16783E+01	0.55233E+02
0.40000E+01	0.25597E+02	0.46378E+02	0.25209E+02	0.28158E+01	0.47378E+02
0.50000E+01	0.20525E+02	0.45361E+02	0.30076E+02	0.40380E+01	0.41186E+02
0.60000E+01	0.16922E+02	0.43797E+02	0.34005E+02	0.52758E+01	0.36183E+02
0.70000E+01	0.14273E+02	0.42058E+02	0.37181E+02	0.64888E+01	0.32057E+02
0.80000E+01	0.12267E+02	0.40321E+02	0.39758E+02	0.76543E+01	0.28601E+02
0.90000E+01	0.10713E+02	0.38664E+02	0.41862E+02	0.87604E+01	0.25665E+02
0.10000E+02	0.94840E+01	0.37122E+02	0.43592E+02	0.98021E+01	0.23144E+02

Table 2.6. Sum of TCE, DCE and VC for each timestep in scenario 3.

Time	TCE+DCE+VC+Ethene
0	100.00
1	100.00
2	100.00
3	100.00
4	100.00
5	100.00
6	100.00
7	100.00
8	100.00
9	100.00
10	100.00

For scenario 3, the results are also verified using the explicit method. The Δt value used for the explicit simulation is 0.001. The simple explicit in time approximation to the reaction Equations 2.21 through 2.25 is:

$$[TCE]_{n+1} = (-k_{tce} * [TCE]_n * [Lactate)_n) * \Delta t + [TCE]_n \tag{2.21}$$

$$[DCE]_{n+1} = (-k_{dce} * [DCE]_n * [Lactate]_n + k_{tce} * [TCE]_n * [Lactate]_n) * \Delta t + [DCE]_n \tag{2.22}$$

$$[VC]_{n+1} = (-k_{vc} * [VC]_n * [Lactate]_n + k_{dce} * [DCE]_n * [Lactate]_n) * \Delta t + [VC]_n \tag{2.23}$$

$$[Ethene]_{n+1} = (k_{vc} * [VC]_n * [Lactate]_n) * \Delta t + [Ethene]_n \tag{2.24}$$

$$[Lactate]_{n+1} = \left(-\left(\frac{1}{2}\right) * k_{tce} * [TCE]_n * [Lactate]_n - \left(\frac{1}{2}\right) * k_{dce} * [DCE]_n * [Lactate]_n - \left(\frac{1}{2}\right) * k_{vc} * [VC]_n * [Lactate]_n\right) * \Delta t + [Lactate]_n \tag{2.25}$$

Figure 2.1 shows the results from the RT3D batch mode calculation match closely the values computed using the explicit method.

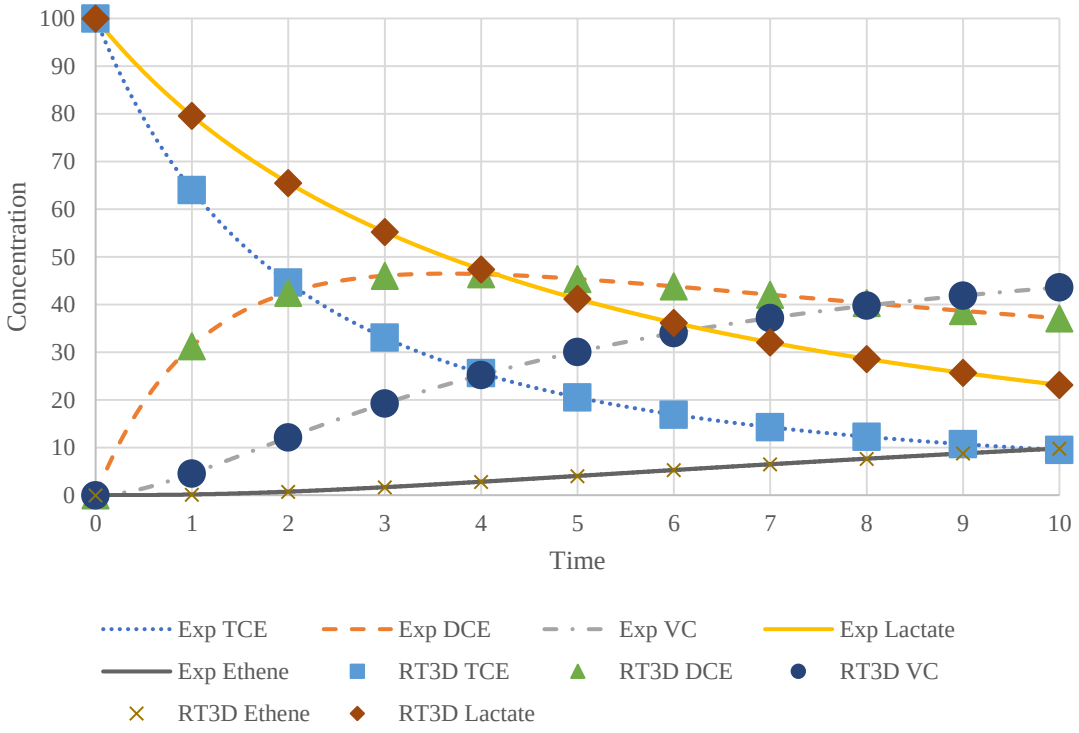

Figure 2.1. Explicit method results in comparison with RT3D batch mode results. Symbols are RT3D, lines are independent numerical solution using explicit in time.

2.5 Testing a Simpler Reductive Dechlorination Model

This section creates a simpler reductive dechlorination model and compares the results with an analytical solution. This simpler case is for sequential linear decay. This is done to dispel the possibility of an error resulting from the interpretation of the compiled dll for the user-defined subroutine in RT3D. Successful results will verify that the compiling instructions in Appendix A are correct. The modeled reaction ordinary differential equations, ODEs, are shown below in Equations 2.26 through 2.28. A description of these rate laws is provided in the RT3D manual (Clement, 1997).

$$\frac{d[TCE]}{dt} = \frac{-k_{tce}[TCE]}{R_{TCE}} \tag{2.26}$$

$$\frac{d[DCE]}{dt} = \frac{-k_{dce}[DCE] + k_{tce}[TCE]}{R_{DCE}} \tag{2.27}$$

$$\frac{d[VC]}{dt} = \frac{-k_{vc}[VC] + k_{dce}[DCE]}{R_{VC}} \tag{2.28}$$

The code below, Table 2.7, is used to compile the dll. The code is compiled as described in Appendix A.

Table 2.7. User defined code describing Equations 2.26 through 2.28.

```
      SUBROUTINE rxns(ncomp,nvrxndata,j,i,k,y,dydt,
     &     poros,rhob,reta,rc,nlay,nrow,ncol,vrc)
c ***** Block 1: Comments block *******
c234567890123456789012345678901234567890123456789012345678901234567890123456789012
c ncomp - Total number of components
c nvrxndata - Total number of variable reaction parameters to be input via RCT file
c J, I, K - node location (used if reaction parameters are spatially variable)
c y - Concentration value of all component at the node [array variable y(ncomp)]
c dydt - Computed RHS of your differential equation [array variable dydt(ncomp)]
c poros - porosity of the node
c reta -  Retardation factor [array variable reta(mcomp)]
c rhob -  bulk density of the node
c rc - Stores spatially constant reaction parameters (up to 100 values)
c nlay, nrow, ncol - Grid size (used only for dimensioning purposes)
c vrc - Array variable that stores spatially variable reaction parameters
c ***** End of Block 1 *******

c *** Block 2: Please do not modify this standard interface block ***
      !MS$ATTRIBUTES DLLEXPORT :: rxns
      IMPLICIT NONE
      INTEGER ncol,nrow,nlay
      INTEGER ncomp,nvrxndata,j,i,k
      INTEGER First_time
      DATA First_time/1/
      DOUBLE PRECISION y,dydt,poros,rhob,reta
```

Table 2.7 (cont.). User defined code describing Equations 2.26 through 2.28.

```
      DOUBLE PRECISION rc,vrc
      DIMENSION y(ncomp),dydt(ncomp),rc(50)
      DIMENSION vrc(ncol,nrow,nlay,nvrxndata),reta(50)
C ****** End of block 2 *******

C *** Block 3: Declare your problem-specific new variables here ***
C     INTEGER
      DOUBLE PRECISION tce,dce,vc,kpce,ktce,kdce,kvc
C ***** End of Block 3  ******

C *** Block 4: Initilize reaction parameters here, if required ***
      IF (First_time .EQ. 1) THEN
        First_time = 0 !reset First_time to skip this block later
      END IF
C ***** End of Block 4  ******

C  *** Block 5: Definition of other variable names ***
       tce = y(1)
       dce = y(2)
       vc = y(3)
       ktce = rc(1)
       kdce = rc(2)
       kvc = rc(3)
C ***** End of Block 5  ******

c  *** Block 6: Definition of Differential Equations ***
       dydt(1) = -ktce*tce/reta(1)
       dydt(2) = (-kdce*dce + ktce*tce)/reta(2)
       dydt(3) = (-kvc*vc + kdce*dce)/reta(3)
C ***** End of Block 6  ******
      RETURN
      END
```

The results from the batch mode are compared with the following analytical solution, where $[TCE]_o$ is the initial TCE concentration, (Tedder and Pohland, 1997). The initial conditions used are 10 mol/l, 0 mol/l, and 0 mol/l for TCE, DCE and VC, respectively.

Additionally, the rate constants used are 0.05 (1/day), 0.03 (1/day), and 0.01 (1/day) for k_{tce}, k_{dce} and k_{vc}.

$$[TCE] = [TCE]_o e^{(-k_{tce}*t)} \tag{2.29}$$

$$[DCE] = \frac{k_{tce} * [TCE]_o}{k_{dce} - k_{tce}} * (e^{-k_{tce}*t} - e^{-k_{dce}*t}) \tag{2.30}$$

$$[VC] = -k_{dce} * k_{tce} * [TCE]_o * \frac{e^{-k_{dce}*t} - e^{-k_{vc}*t}}{(k_{vc} - k_{dce}) * (k_{dce} - k_{tce})} + k_{dce} * k_{tce} * [TCE]_o * \frac{e^{-k_{tce}*t} - e^{-k_{vc}*t}}{(k_{vc} - k_{tce}) * (k_{dce} - k_{tce})} \tag{2.31}$$

During the batch utility run the following parameters are used: ncomp equals 3, no_of_timesteps equals 100, delt equals 1. The initial concentration values are as follows: 10, 0, 0 for TCE, DCE and VC respectively. Additionally, default tolerances are used. The following three rate constants are entered for k_{tce}, k_{dce} and k_{vc}: 0.05, 0.03, and 0.01. Lastly, all concentrations are assumed to be in moles/liter, the rate constants in 1/(day) and time is in days.

The results from the simpler TCE reductive dechlorination model matched the results generated using analytical solution, Equations 2.29 through 2.31. This was done to provide a secondary verification that the RT3D batch mode accurately interpreted the compiled dll file. The results from the simpler model agree with the values from the analytical solution, shown in Figure 2.2, thus verifying the compiling procedures and the subsequent interpretation of the compiled dll by RT3D.

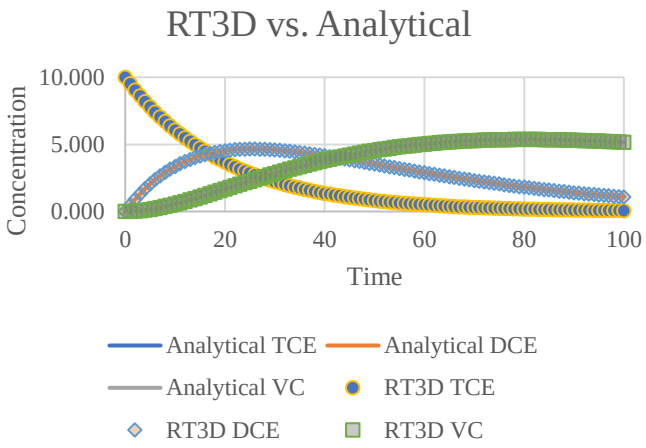

Figure 2.2. RT3D batch utility solution in comparison with the analytical solution. Symbols are the RT3D results whereas lines are the analytical solution.

2.6 Simulating Two-Dimensional Flow Cell Using Lactate/TCE model

This section will simulate a typical treatment scenario where lactate is introduced to the subsurface to promote the biological decay of TCE using the lactate/TCE chemistry shown in Section 2.2. The modeled flow cell is based on an experimental flow cell created by Erin Berns at University of Texas, Austin (Erin Berns, University of Texas, Austin, Personal Communication, 2016). In addition, all computer modeling is done using GMS version 10.2.

The physical dimensions of the modeled flow cell are 17.5 inches in the x direction, 0.79 in in the y direction and 19.5 inches in the z direction. The grid dimension is 35 X 1 X 42 cells in the x, y and z direction, where x and y direction cells are uniform. Additionally, the flow cell is divided into a high permeability zone (HPZ) and a low permeability zone (LPZ). This simulates the effects of back diffusion and the heterogeneity of the subsurface. The isotropic hydraulic conductivity of the HPZ and LPZ are 34.015 in/day and 0.00340157 in/day., respectively. The porosity equals 0.31 for the HPZ and 0.06 for LPZ. These porosities are the ones used to estimate the flow in the experimental flow cell (Erin Berns, University of Texas, Austin, Personal

Communication, 2016). Lastly for the flow model, solved using MODFLOW, there are two constant head boundaries with values of 25 in on the left and 24.5 in on the right side of the HPZ. These values were chosen so that lactate will move faster through the HPZ and then diffuse in to the LPZ; the lactate boundary condition is discussed later. This effectively simulates the experimental flow cell where the flow mostly occurs in the HPZ. The LPZ is surrounded by no flow boundaries. Figure 2.3 shows the flow model setup. The flow model is solved in steady state mode.

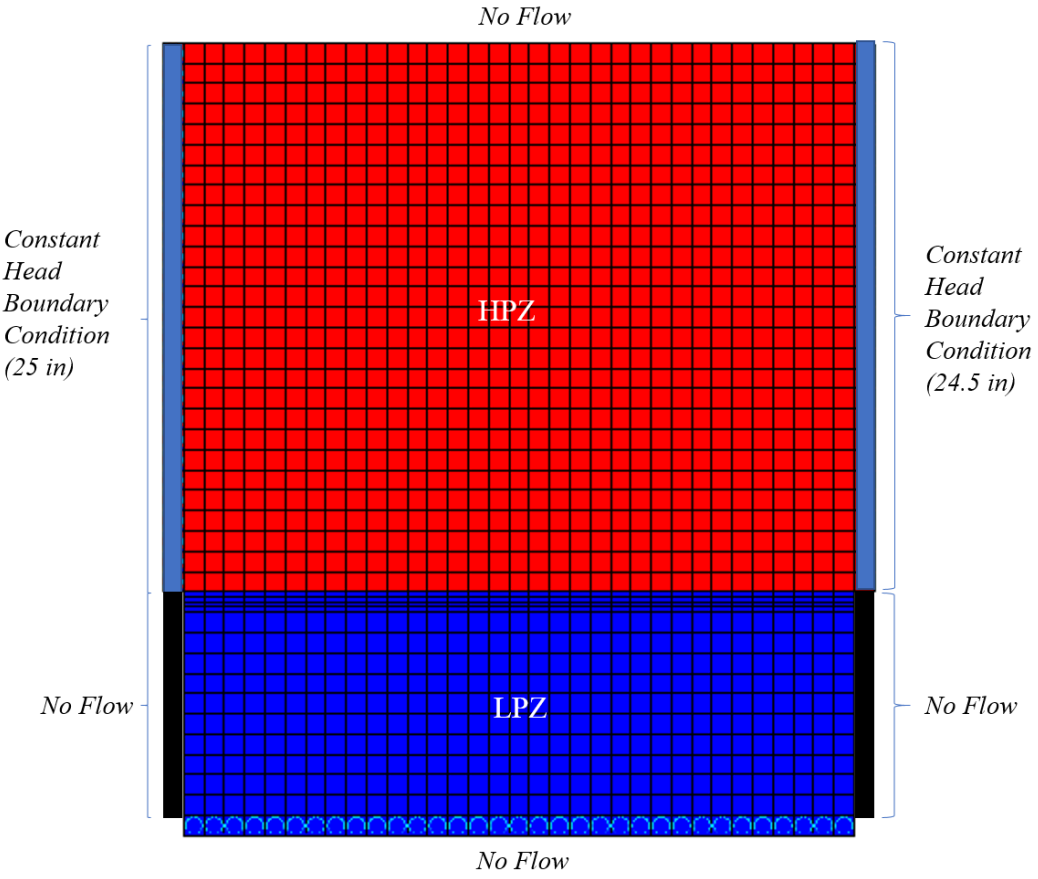

Figure 2.3. Flow model setup, used by MODFLOW.

While the MODFLOW simulation computes the groundwater flow velocity, the contaminant fate and transport is solved using RT3D. Five species are added to simulation, TCE

(1), DCE (2), VC (3), ethene (4) and lactate (5). All species have an initial condition of 0.0 moles/liter. The simulation period is 250 days. The diffusion coefficient is set at 0.04874698 in^2/day, whereas all dispersivity values are set to zero. The diffusion coefficient is based on the one used to estimate the flow in the experimental flow cell (Erin Berns, University of Texas, Austin, Personal Communication, 2016). Additionally, although we would expect significant mechanical dispersion in a real system, this model mainly focuses on the LPZ where diffusion dominates. Therefore, this model ignores mechanical dispersion. Furthermore, to limit the effects of numerical dispersion resulting from the lack of mechanical dispersion, the advection and dispersion are solved using the total variation diminishing (TVD) option in RT3D. TVD has been shown to perform well under high advection problems; details are presented in the MT3D manual (Zheng et al.,1999). The constant concentration boundary conditions, shown in Figure 2.4, are set at 0.009 moles/liter for TCE and 0.001 moles/liter for lactate. In Figure 2.4, at the location of the lactate boundary condition, only 0.001 mol/l lactate is present whereas boundary conditions for other chemicals, TCE, DCE, VC and ethene, are set at 0.0 mol/l. Similarly, at the TCE boundary condition at the bottom of the flow cell only 0.009 mol/l TCE is present whereas the boundary conditions for the other chemicals is 0.0 mol/l. In addition, the LPZ is surrounded by no flux boundaries and the HPZ at the exit nodes is zero gradient boundary. The mass removed at the HPZ exit boundary is equal to the flow entering the system multiplied by the concentration at the cells (Zheng et al., 1999). These boundary conditions were set to be similar to the ones in the experimental flow cell. The rate constants used are 432 L/(mol*day), 259.2 L/(mol*day), and 86.4 L/(mol*day) for ktce, kdce and kvc, respectively. These rate constants are only applied to the LPZ, thus simulating TCE decay resulting only from the lactate diffusion into the LPZ. The rate constants were arbitrarily chosen to show the formation of ethene in a

reasonable time frame. The general Gear solver is used to solve the user defined subroutine; see details in the RT3D manual (Clement, 2002). Table 2.8 contains a summary of all the model parameters. Lastly, no sorption is modeled and therefore the listed bulk density of 1600000 g/in^3 is not used in the simulation.

Table 2.8. Summary of MODFLOW and RT3D model parameters used in the 2D Flow Cell Simulations.

Parameter	Value	Units
Simulation Time Length	250	Day
Diffusion Coefficient	0.04874698	in^2/day
Dispersivity	0	in
HPZ porosity	0.31	Unitless
LPZ porosity	0.06	Unitless
Ktce	432	Liter/(mol*day)
Kdce	259.2	Liter/(mol*day)
Kvc	86.4	Liter/(mol*day)
HPZ hydraulic conductivity	34.015	in/day
LPZ hydraulic conductivity	0.00340157	in/day
Bulk density	1600000.0	g/in^3

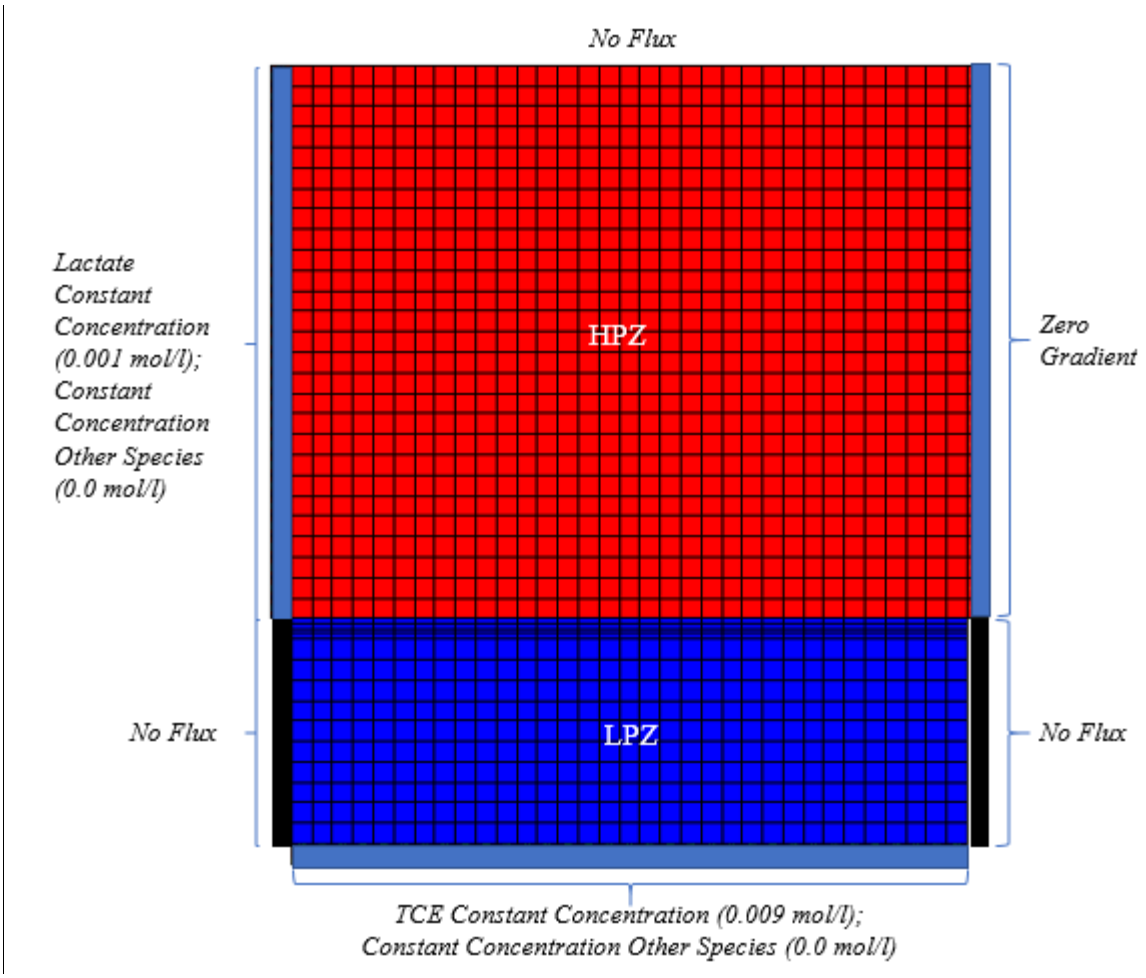

Figure 2.4. Boundary Conditions, BC, used in RT3D simulation.

Detailed model setup instructions using GMS version 10.2 for the MODFLOW model are provided in Appendix B.1 and for RT3D in Appendix B.2.

2.7 Two-Dimensional Simulation Results and Discussion

This section contains the results and discussion for the simulation setup described in Section 2.6. Results from the MODFLOW simulation are in Figure 2.5. MODFLOW simulation shows that most of the flow occurs in the HPZ although limited amount is present in the LPZ. Given the head gradient and porosity for the HPZ, the flow velocity is approximately constant and equal to 3.14 in/day; there is limited flow in the LPZ. The HPZ velocity is calculated as:

$$v = -\frac{34.015\,\frac{in}{day}}{0.31} * \frac{24.5\ in - 25.0\ in}{17.5\ in} = 3.14\ in/day$$

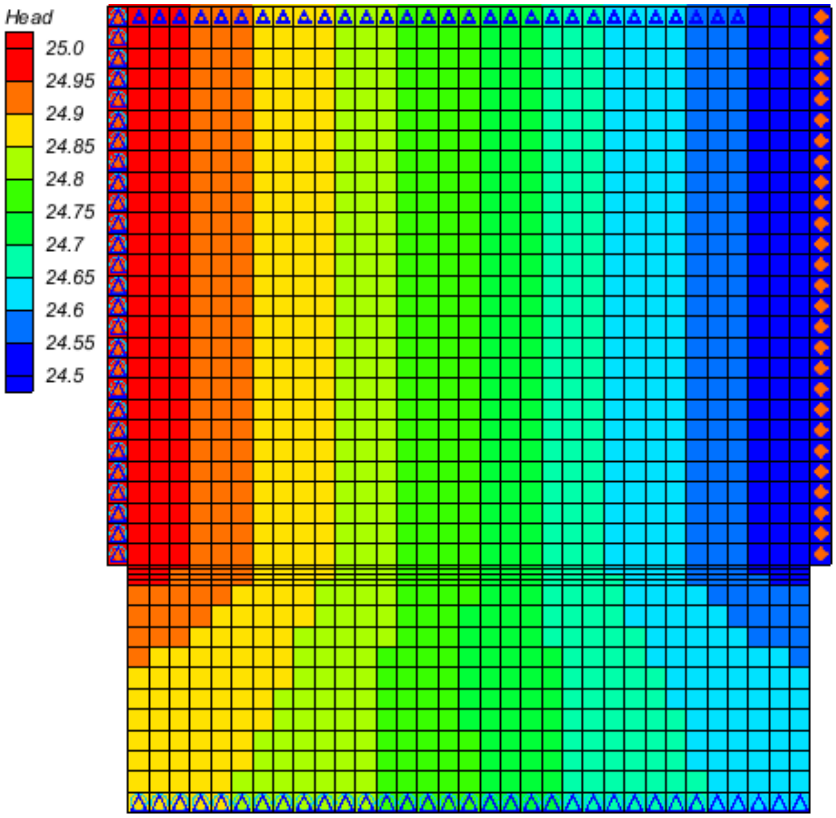

Figure 2.5. Head contours solved using MODFLOW in steady state mode. The boundary condition on the left is set at a constant head of 25 in while on the right at 24.5 in. Head contours indicate majority of the flow occurs in the HPZ although some is present in the LPZ.

TCE, Lactate, DCE, VC and ethene concentration results are presented at 25 days, 125 days and the end of simulation at 250 days. The timesteps are automatically calculated by RT3D to meet stability conditions with the first time step being 0.1539024 days. Additionally, concentration profiles of TCE and lactate in cases with no decay case are also presented. This is done in order to better understand TCE degradation resulting from the lactate/TCE interaction,

chemical reactions R2.1 through R2.3. The no decay results are calculated by setting all the rate constants equal to zero, thus effectively creating a tracer.

Figures below indicate that TCE was successfully decayed using lactate as a donor in the 2-D flow cell. Additionally, the chapter goals of creating a user defined RT3D package to model a lactate/TCE interaction were also met. The 2D flow cell model, Figures 2.6 through 2.22, accurately showed the formation of DCE, VC and ethene as lactate continued to diffuse into the LPZ. This is especially seen when comparing the decay with the no decay concentration profiles of TCE and Lactate, Figures 2.8, 2.9 and Figures 2.12, 2.13, respectively. These figures compare the concentration profiles for decay and no decay case at 250 days. In Figure 2.8, TCE diffused to a lower distance when compared with no decay case, Figure 2.9. Similarly, for lactate, the no decay case diffuses further into the LPZ, Figure 2.13, as opposed to the case decay case, Figure 2.12, thus highlighting the usage of lactate and TCE to form DCE, VC and ethene. Lactate consumption to form TCE degradation productions is also seen when comparing the lactate concentration profiles over time; the concentration profiles decrease with depth into the LPZ when comparing day 25, 125 and 250, Figures 2.10, 2.11 and 2.12. The formation of DCE is seen in the progression of the concentration profiles from day 25 through 250, Figures 2.14 through 2.16. Similarly, formation of VC and ethene over time is seen in Figures 2.17 through 2.19 and Figures 2.20 through 2.22, respectively. The sequential nature of formation of DCE to VC to ethene is noticed when comparing the peak concentration for each: DCE peak concentration is around 0.0006 mol/l, Figure 2.16, VC peak concentration 0.0003 mol/l, Figure 2.19, and ethene is 0.00009 mol/l, Figure 2.22.

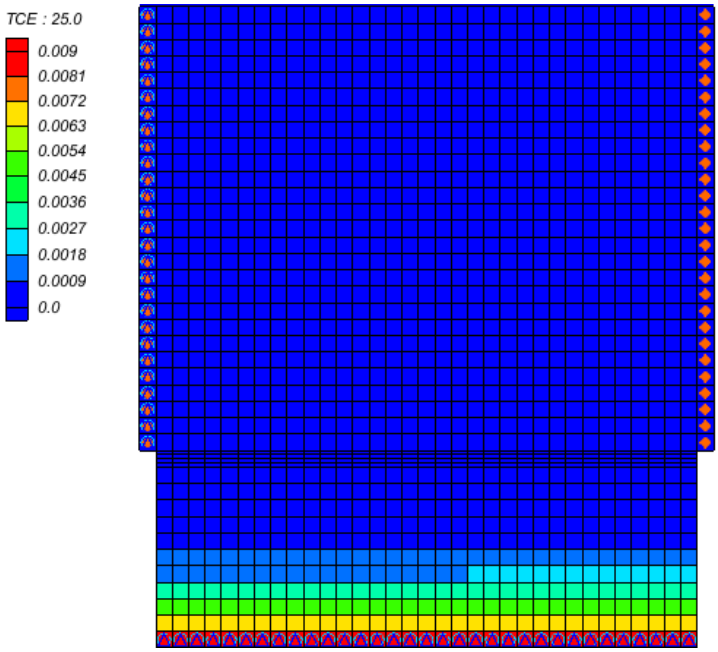

Figure 2.6. TCE concentration profile at 25 days; all concentrations are in moles/liter.

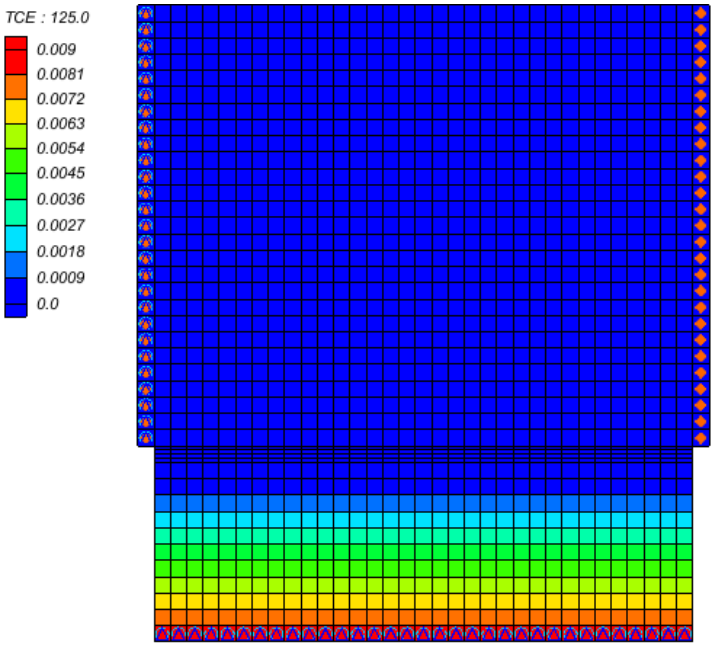

Figure 2.7. TCE concentration profile at 125 days; all concentrations are in moles/liter.

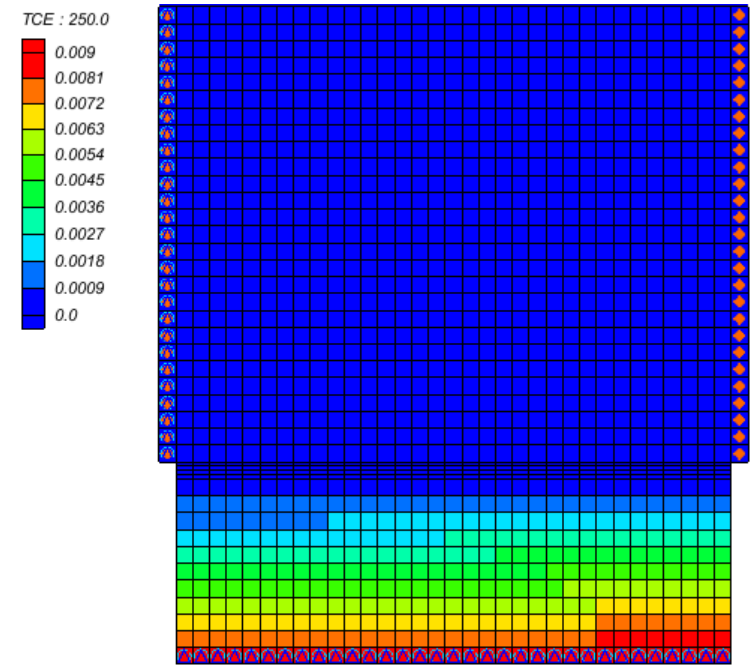

Figure 2.8. TCE concentration profile at 250 days; all concentrations are in moles/liter.

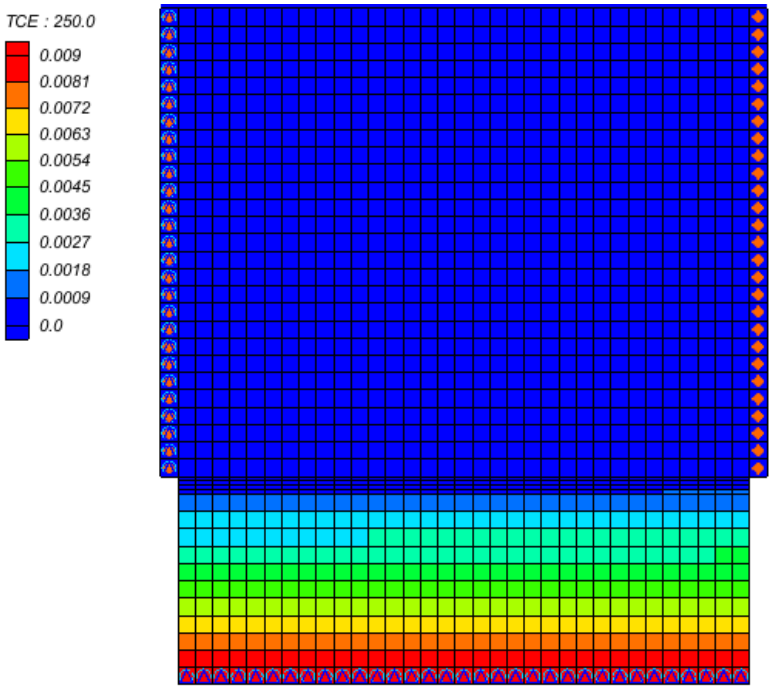

Figure 2.9. TCE profile at 250 days if no decay occurs; all concentrations are in moles/liter.

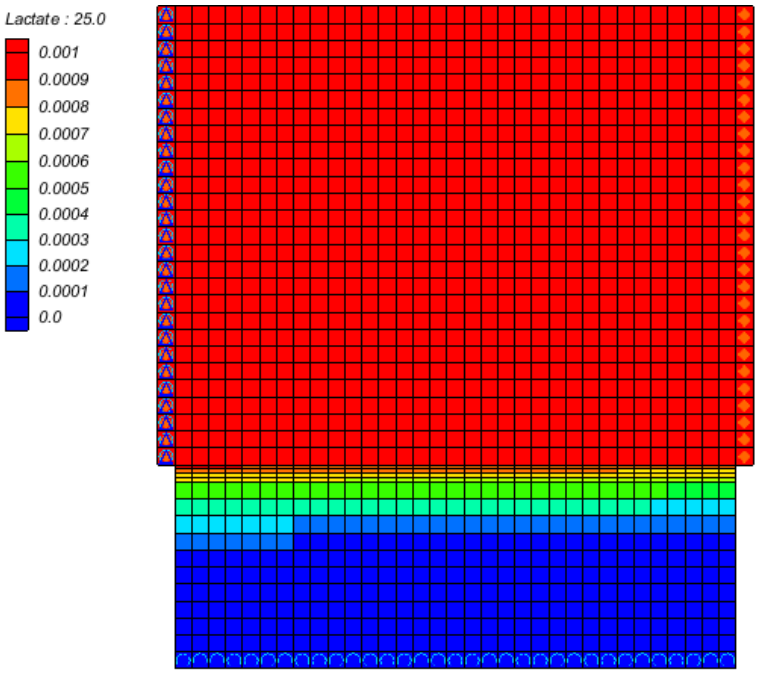

Figure 2.10. Lactate concentration profile at 25 days; all concentrations are in moles/liter.

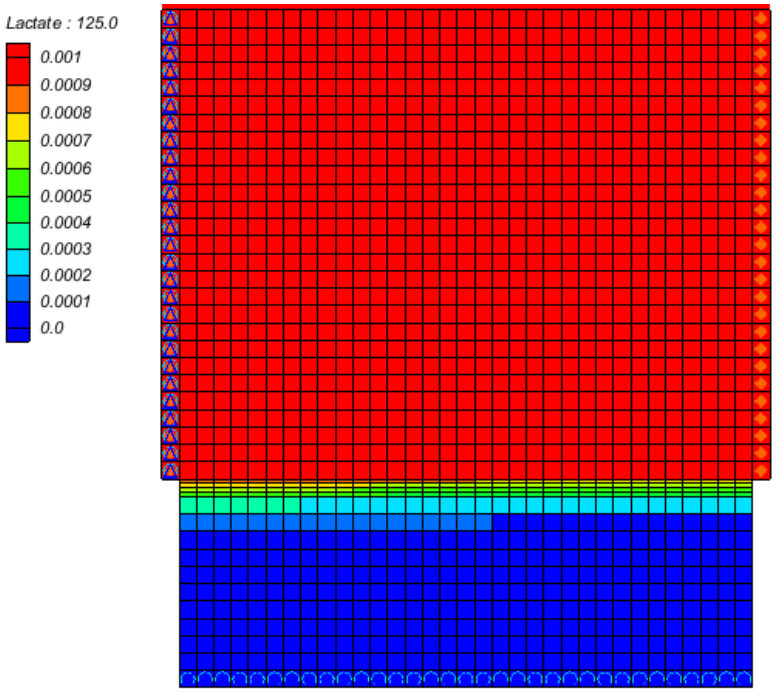

Figure 2.11. Lactate concentration profile at 125 days; all concentrations are in moles/liter.

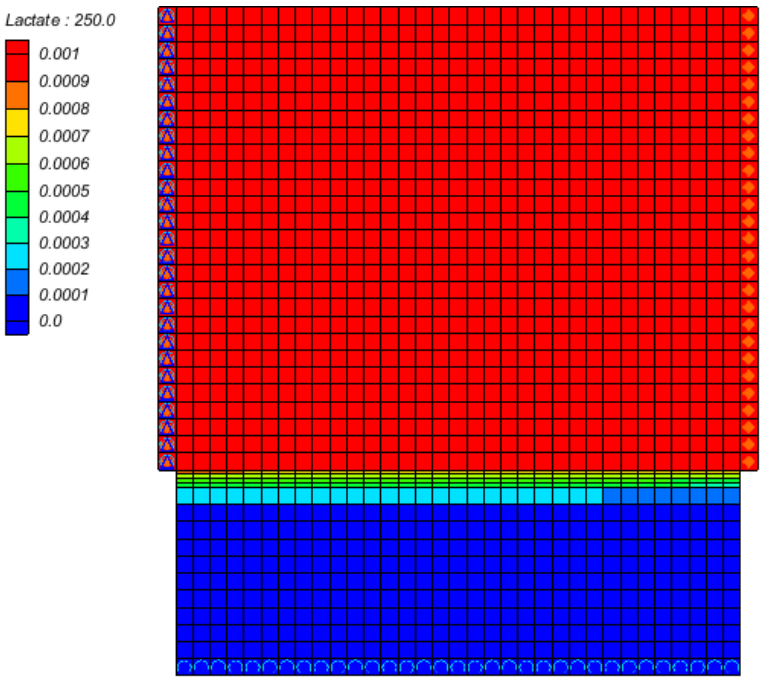

Figure 2.12. Lactate concentration profile at the end of simulation (250 days); all concentrations are in moles/liter.

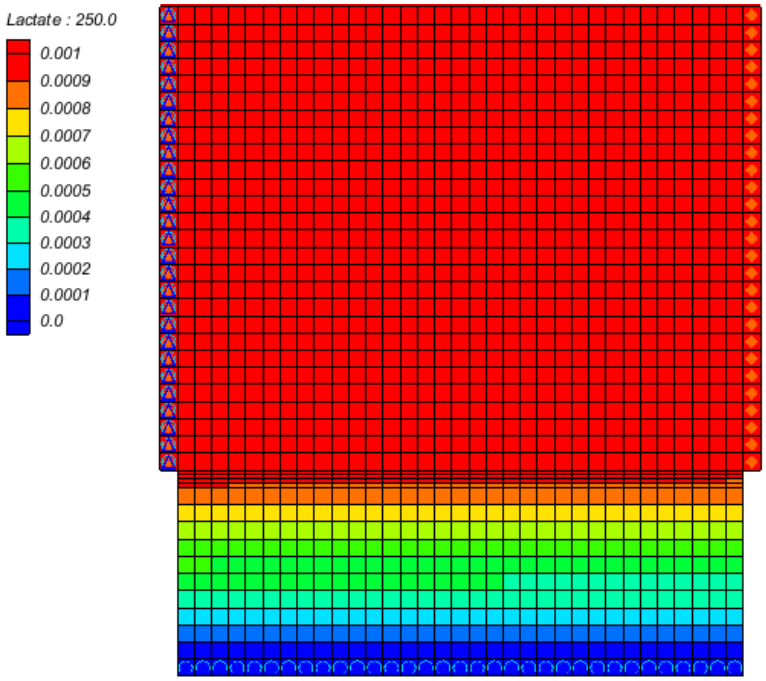

Figure 2.13. Lactate profile if no decay occurs at 250 days; all concentrations are in moles/liter.

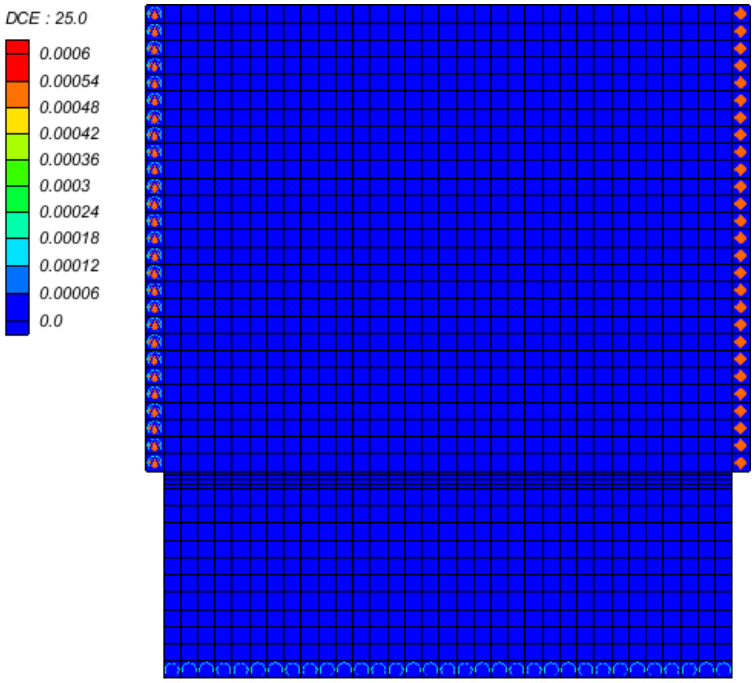

Figure 2.14. DCE concentration profile at 25 days; all concentrations are in moles/liter.

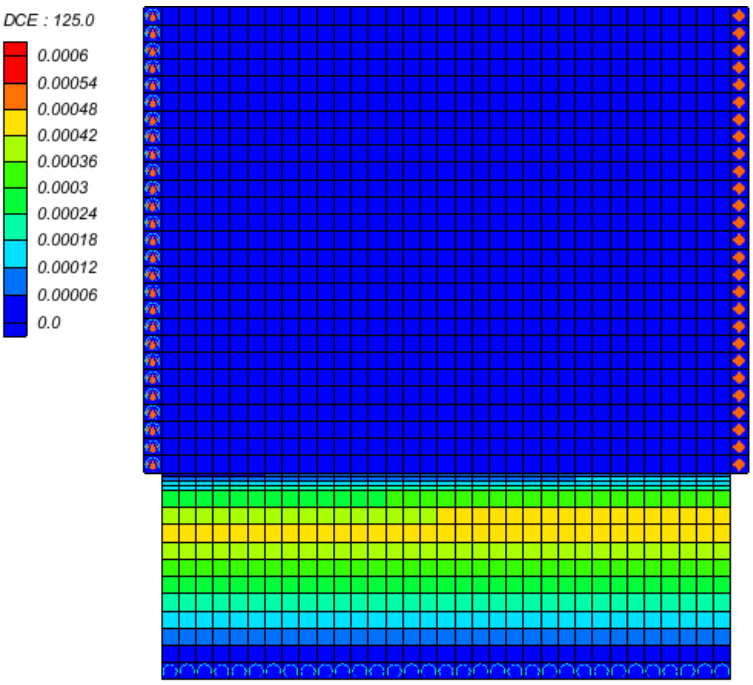

Figure 2.15. DCE concentration profile at 125 days; all concentrations are in moles/liter.

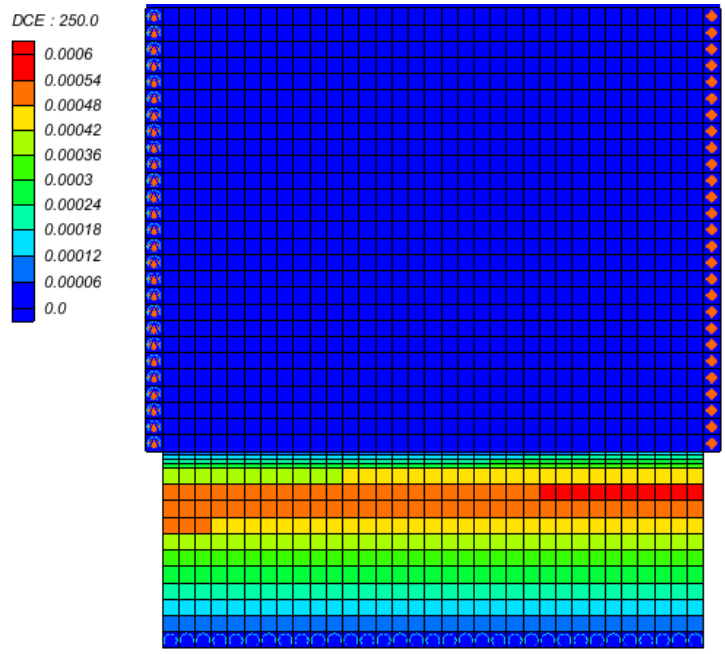

Figure 2.16. DCE concentration profile at 250 days; all concentrations are in moles/liter.

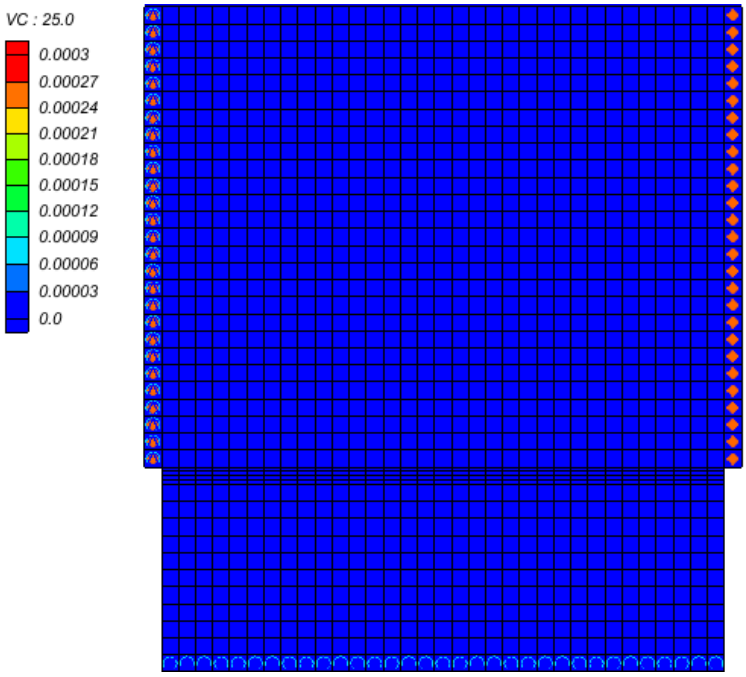

Figure 2.17. VC concentration profile at 25 days; all concentrations are in moles/liter.

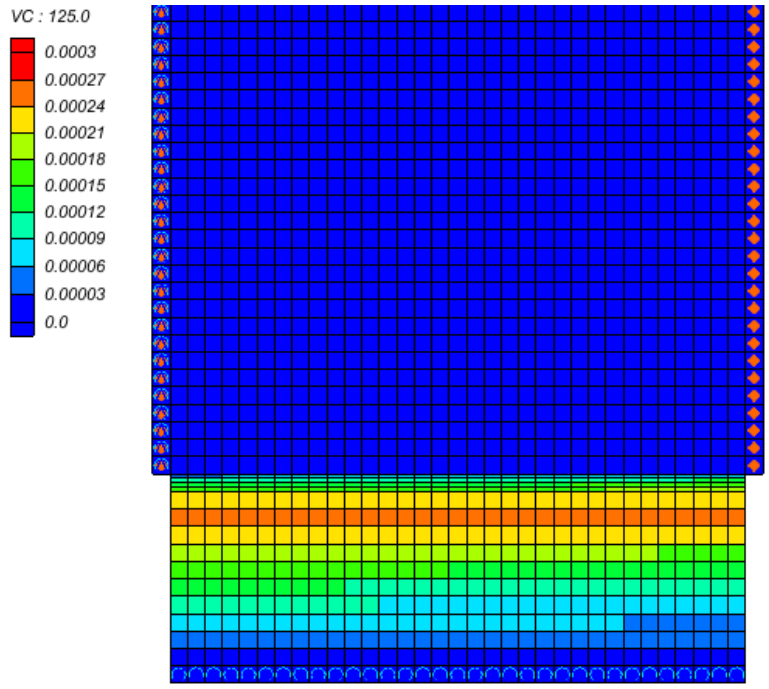

Figure 2.18. VC concentration profile at 125 days; all concentrations are in moles/liter.

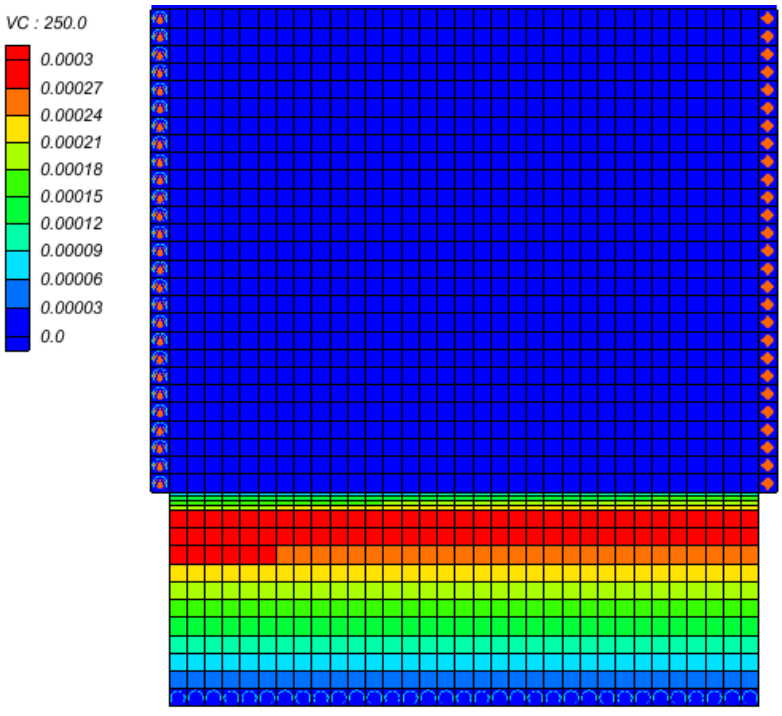

Figure 2.19. VC concentration profile at 250 days; all concentrations are in moles/liter.

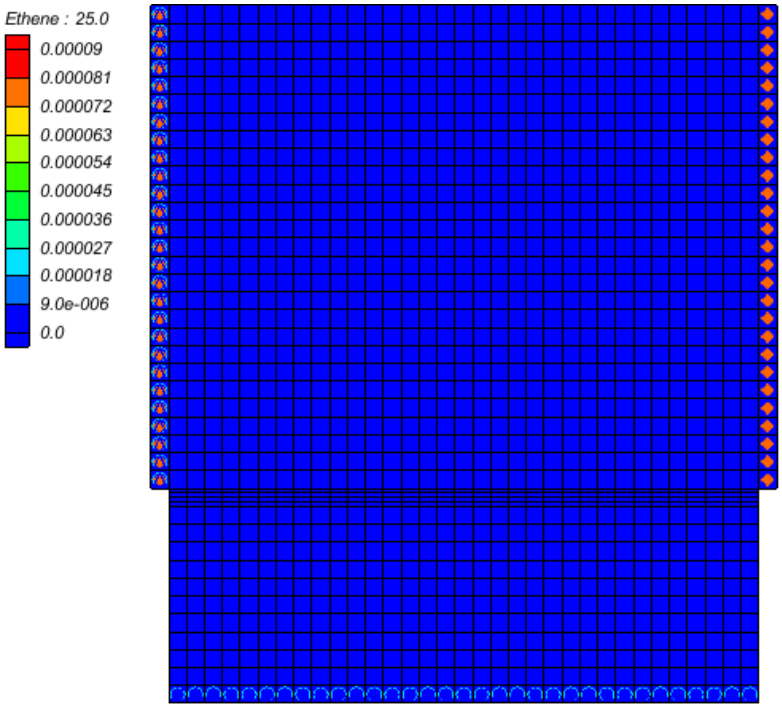

Figure 2.20. Ethene concentration profile at 25 days; all concentrations are in moles/liter.

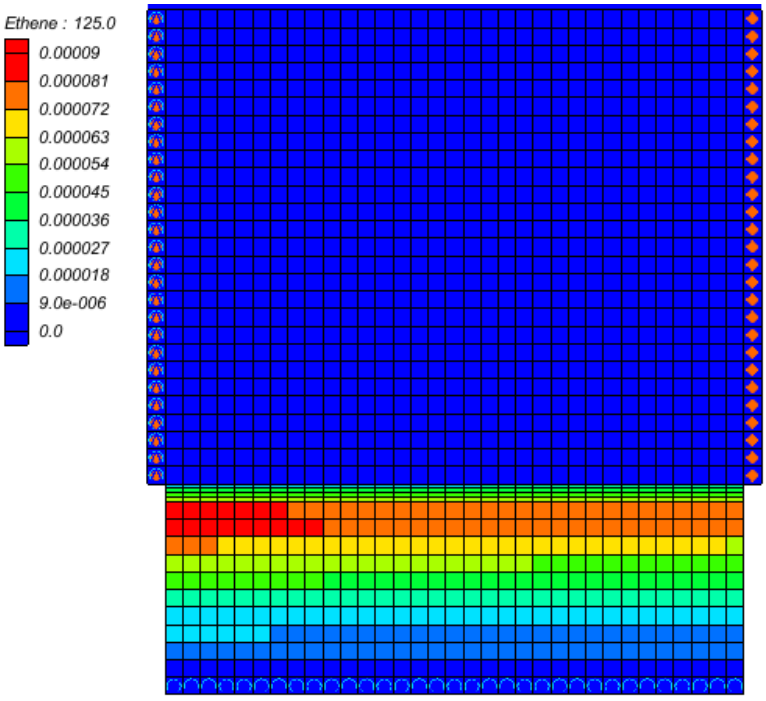

Figure 2.21. Ethene concentration profile at 125 days; all concentrations are in moles/liter.

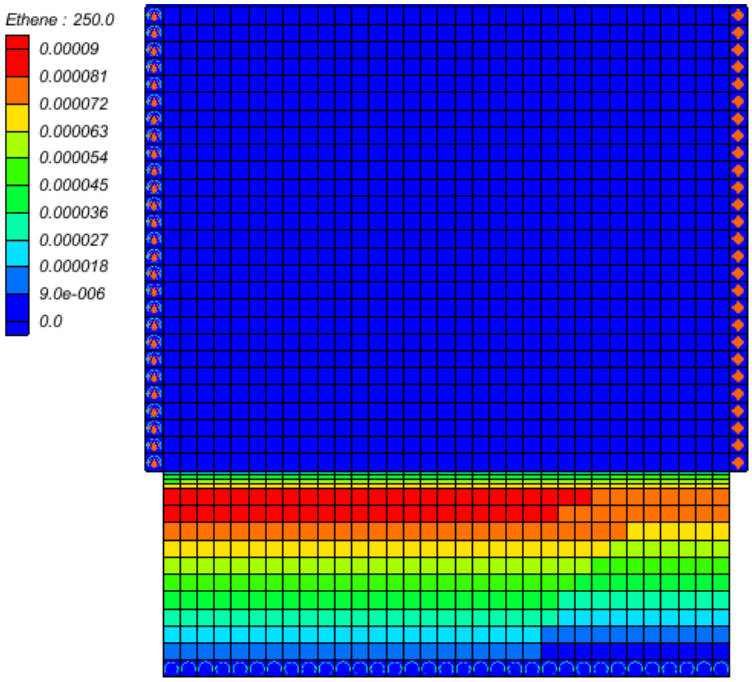

Figure 2.22. Ethene concentration profile at the end of simulation (250 days); all concentrations are in moles/liter.

Concentration profiles across the column 17 for all layers in the LPZ are provided below in Figures 2.23 through 2.26. The location for the concentration profile is shown in Figure 2.28. These concentration profiles successfully showed that enough quantities of lactate and TCE were present to facilitate the transformation of TCE. These profiles also showed that only marginally higher amounts of DCE, VC and ethene were formed between day 125 and 250, due the limited amount of lactate remaining in the system, Figures 2.25 and 2.26. Additionally, these figures also highlight that the model sequentially formed DCE, VC, and then ethene: Figure 2.23 at the first time step of the simulation showed no transformation of TCE into daughter products, whereas Figure 2.24 at day 25 only showed the formation of DCE and lastly Figures 2.25 and 2.26 at days 125 and 250 showed the formation of all TCE products.

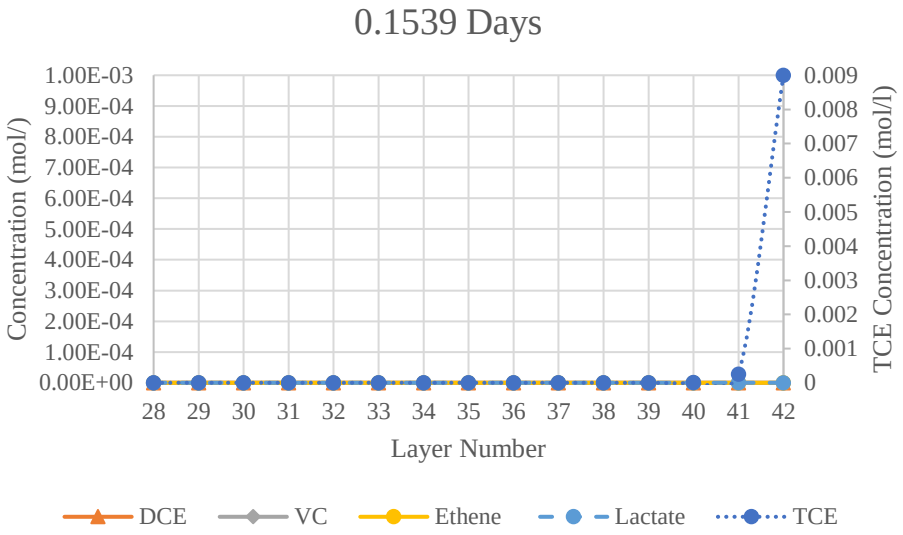

Figure 2.23. Concentration profile across column 17 of the LPZ (see Fig. 2.28) at the first time step of the simulation. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

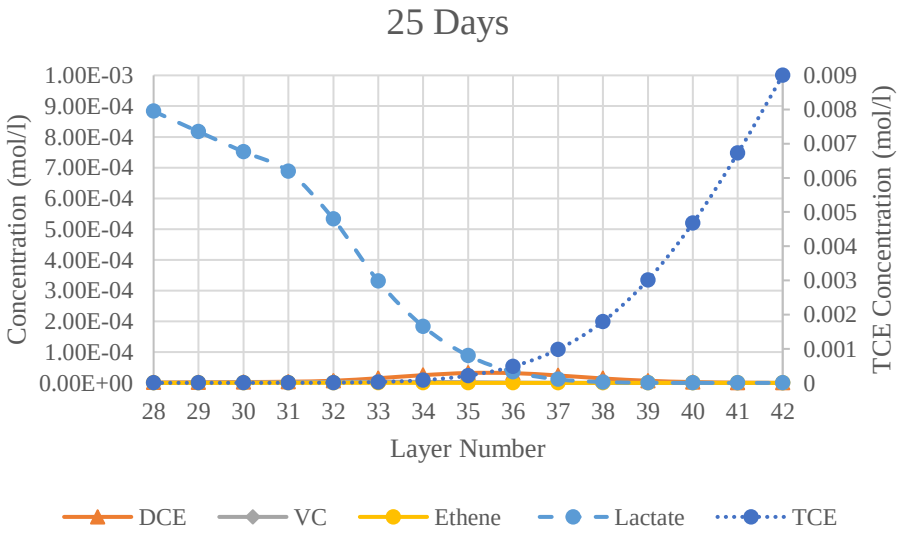

Figure 2.24.Concentration profile across column 17 of the LPZ (see Fig. 2.28) at 25 days. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

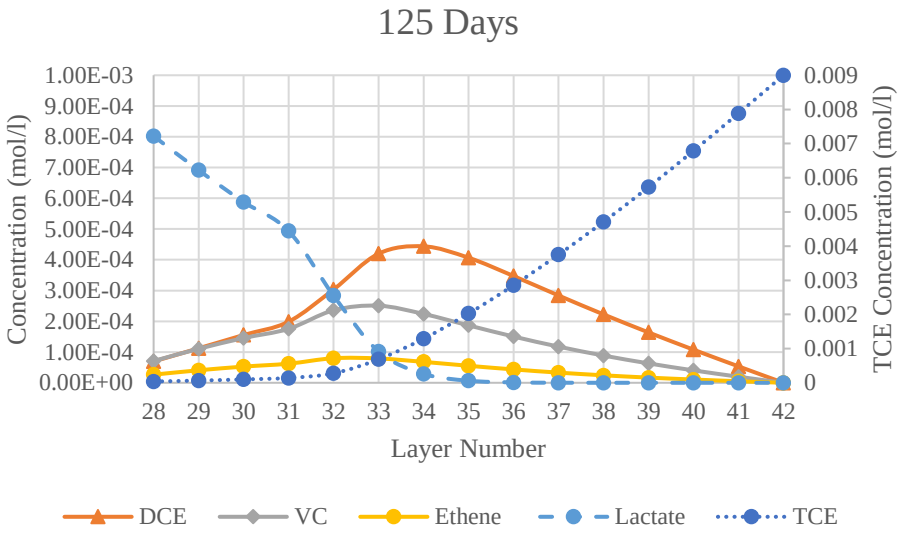

Figure 2.25. Concentration profile across column 17 of the LPZ (see Fig. 2.28) at 125 days. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

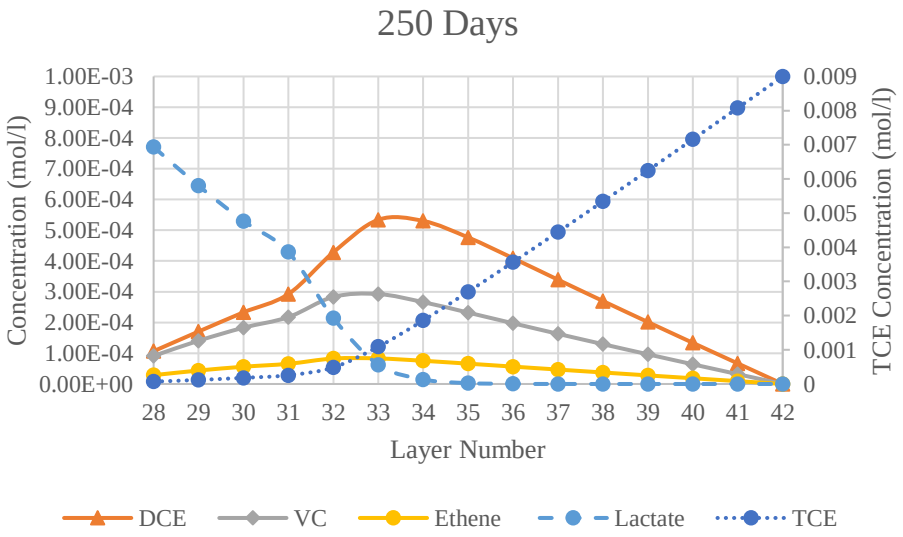

Figure 2.26. Concentration profile across the column 17 of the LPZ (see Fig. 2.28) at 250 days. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

Lastly, TCE breakthrough curve at the first exit node at the HPZ-LPZ interface is shown below, Figure 2.27. This figure compares the TCE concentration in the decay scenario in

comparison with the no decay scenario. The breakthrough curves indicate the mitigation in the effects of back diffusion resulting from the biotic reactions occurring in the LPZ in the presence of lactate; the no decay case having a higher concentration of TCE back diffuse into the HPZ as opposed to the case where TCE transformations occurred. Finally, Figure 2.28 summarizes the cells used in calculating the concentration profiles in Figures 2.23 through 2.26 and the location where the breakthrough curve is calculated in Figure 2.27.

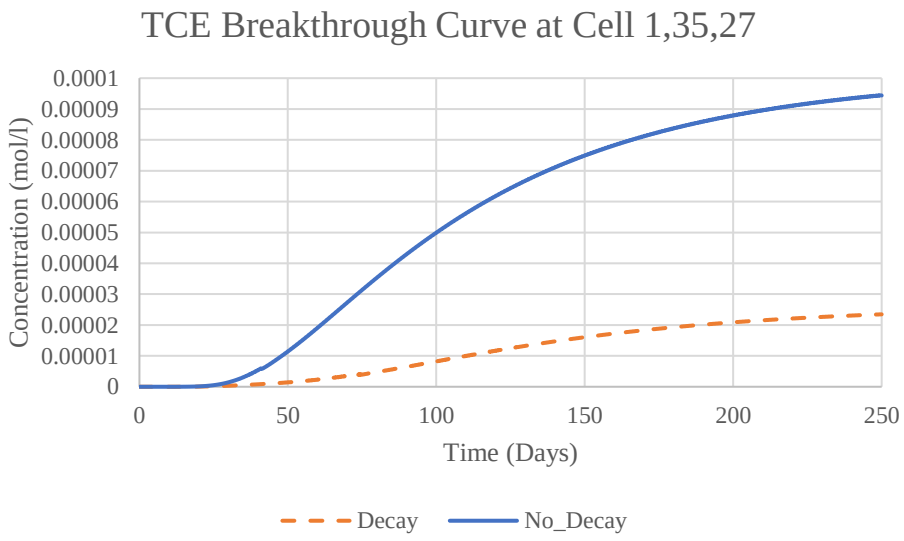

Figure 2.27. TCE breakthrough curve at the selected cell 1,35,27 (see Fig. 2.28).

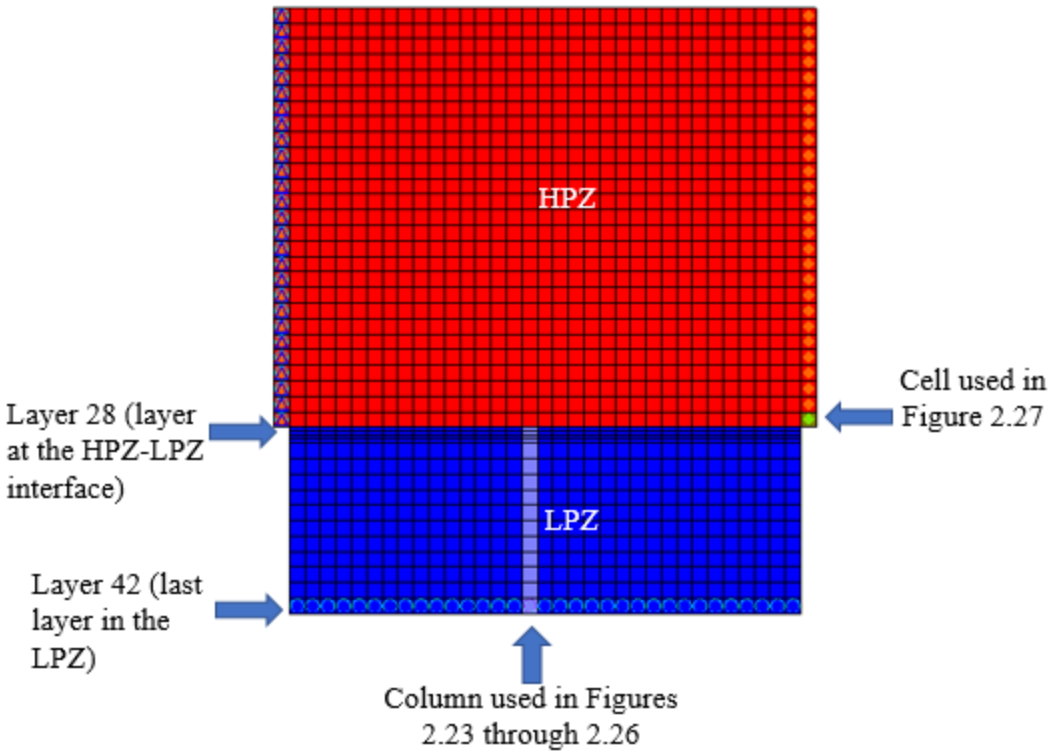

Figure 2.28. Figure indicates the locations in the simulated flow cell used for calculating the concentration profiles in Figures 2.23 through 2.26 and Figure 2.27.

2.8 Closing Remarks

This chapter demonstrates how to incorporate user-defined reaction modules into RT3D. We developed the TCE/lactate model for sequential reductive dechlorination of TCE using lactate as the electron donor. Several assumptions were made in the creation of the lactate/TCE model, the most important of which was the assumption of second order rate behavior for chlorinated solvent decay. It is important to note that this model should not be used unless the field results indicate the same chemistry and rate laws as described in Section 2.2. Additionally, this chapter assumed rate constants which may differ from field conditions; prior to usage of this model the user should also estimate the rate constants based on field conditions.

Chapter 3. Model Development for Abiotic and Biotic Transformation of TCE

Several lab studies have indicated that abiotic reactions affect the fate of TCE in LPZs. A study conducted by Hayes and Butler (1999) showed that FeS can abiotically transform TCE into acetylene. Another study indicated that presence of ferrous minerals in rock matrices, i.e. LPZ, can result in significant decay of TCE and mitigate the effects of back diffusion (Schaefer et al., 2013). This chapter will present a model for the transformation of TCE using abiotic reactions coupled with the biotic reactions presented in Chapter 2.

3.1 System Chemistry

As indicated in Chapter 1, TCE can be degraded abiotically. This can occur if there are reduced iron minerals in the LPZ, since reduced iron can serve as an electron donor, reacting with TCE to form acetylene and oxidized iron (see the studies cited above). Since reduced and oxidized iron can form minerals and iron geochemistry can be quite complicated, in this chapter we will neglect these geochemical processes that can change pH and iron speciation and simply assume that iron is present in the form of Fe(red) and Fe(ox), reduced and oxidized, respectively. A similar approach has been taken by others in literature when modeling BTEX degradation under iron reducing conditions (Liu et al, 1999; Clement, 1997). Another simplification is made by assuming that TCE degrades to directly form acetylene. Studies have indicated that typically TCE degrades to form the intermediate chloro-acetylene followed by acetylene, but chloro-acetylene decays relatively quickly into acetylene (Roberts et al.,1996; Arnold and Roberts, 2000). Therefore, the transformation of TCE directly into acetylene is assumed to be a reasonable assumption. The chemical reaction for such a system is as follows:

$$C_2HCl_3 + Fe(red) \rightarrow C_2H_2 + Fe(ox) \quad \text{(R3.1)}$$

Assuming second-order rate laws, the rate laws corresponding to this chemical reaction can be conceptually represented as follows:

$$\frac{d[Acetylene]}{dt} = k_{tcefe} * [TCE] * [Fe(red)] \quad (3.1)$$

$$\frac{d[Fe(red)]}{dt} = -k_{tcefe} * [TCE] * [Fe(red)] \quad (3.2)$$

$$\frac{d[Fe(ox)]}{dt} = k_{tcefe} * [TCE] * [Fe(red)] \quad (3.3)$$

$$\frac{d[TCE]}{dt} = -k_{tcefe} * [TCE] * [Fe(red)] \quad (3.4)$$

It is also important to note that chemical reaction R3.1 is extremely simplified and Fe(red) and Fe(ox) may be in solid phase, this study is assuming all concentrations are in equivalent moles/liter.

For the case where lactate is added as an electron donor to stimulate biotic reduction of TCE, there is also the possibility that iron-reducing bacteria could use lactate. Therefore, another mechanism is also added to system, during which Fe(ox) is used with lactate to form Fe(red). The simplified chemical reaction of this mechanism is as follows:

$$Fe(ox) + CH_3CHOHCOO^- \rightarrow Fe(red) \quad \text{(R3.2)}$$

Equation R3.2 indicates that iron reducing bacteria competes with the dechlorinating bacteria in the coupled system, since both the biotic reactions in Chapter 2 and the Equation R3.2 use lactate as an electron donor. Additionally, several assumptions are made in both R3.1 and

R3.2, in that the equations are not in their balanced form. In both equations, all the products formed are not displayed due to lack of reaction stoichiometry.

Table 3.1. Chemical formula and the corresponding name of compounds used in reactions R3.1. and R3.2.

Chemical Formula	Name
C_2HCl_3	Trichlorethylene (TCE)
C_2H_2	Acetylene
$CH_3CHOHCOO^-$	Lactate

The corresponding second order rate laws are:

$$\frac{d[Fe(red)]}{dt} = k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.5)$$

$$\frac{d[Fe(ox)]}{dt} = -k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.6)$$

$$\frac{d[Lactate]}{dt} = -k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.7)$$

3.2 Coupling Abiotic and Biotic Systems.

This section will couple the abiotic rate laws, Section 3.1, and the biotic rate laws, Section 2.2, to form a coupled biotic and abiotic system. The second-order rate laws for the coupled system will become:

$$\frac{d[TCE]}{dt} = -k_{tce}[TCE] * [Lactate] - k_{tcefe} * [TCE] * [Fe(red)] \quad (3.8)$$

$$\frac{d[DCE]}{dt} = -k_{dce}[DCE] * [Lactate] + k_{tce}[TCE] * [Lactate] \quad (3.9)$$

$$\frac{d[VC]}{dt} = -k_{vc}[VC] * [Lactate] + k_{dce}[DCE] * [Lactate] \quad (3.10)$$

$$\frac{d[Ethene]}{dt} = k_{vc}[VC] * [Lactate] \quad (3.11)$$

$$\frac{d[Lactate]}{dt} = -\left(\frac{1}{2}\right) * k_{tce} * [TCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{dce} * [DCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{vc} * [VC] * [Lactate] - k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.12)$$

$$\frac{d[Acetylene]}{dt} = k_{tcefe} * [TCE] * [Fe(red)] \quad (3.13)$$

$$\frac{d[Fe(red)]}{dt} = -k_{tcefe} * [TCE] * [Fe(red)] + k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.14)$$

$$\frac{d[Fe(ox)]}{dt} = k_{tcefe} * [TCE] * [Fe(red)] - k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.15)$$

Additionally, the partial differential equations for the coupled system are shown below, Equations 3.16 through 3.23. The terms of the advection-dispersion-reaction equation used in this section have been defined in Chapter 2. Fe(red) is treated as an immobile species because it is mostly expected to be in the form of minerals, and as such the partial differential equation is modified to only contain the reaction term. Fe(ox) is treated as a mobile species because the reduction of Fe(red) may generate Fe(ox) in aqueous form.

$$R_{TCE}\frac{\partial([TCE])}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\left(\frac{\partial[TCE]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(v_i[TCE]) + \frac{q_s}{\theta}[\mathrm{TCE}]_s - k_{tce}[TCE] * [Lactate] - k_{tcefe} * [TCE] * [Fe(red)] \quad (3.16)$$

$$R_{DCE}\frac{\partial([DCE])}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\left(\frac{\partial[DCE]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(v_i[DCE]) + \frac{q_s}{\theta}[\mathrm{DCE}]_s - k_{dce}[DCE] * [Lactate] + k_{tce}[TCE] * [Lactate] \quad (3.17)$$

$$R_{VC}\frac{\partial([VC])}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\left(\frac{\partial[VC]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(v_i[VC]) + \frac{q_s}{\theta}[\mathrm{VC}]_s - k_{vc}[VC] * [Lactate] + k_{dce}[DCE] * [Lactate] \quad (3.18)$$

$$R_{Ethene}\frac{\partial([Ethene])}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\left(\frac{\partial[Ethene]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(v_i[Ethene]) + \frac{q_s}{\theta}[\mathrm{Ethene}]_s + k_{vc}[VC] * [Lactate] \quad (3.19)$$

$$R_{Lactate}\frac{\partial([Lactate])}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\left(\frac{\partial[Lactate]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(v_i[Lactate]) + \frac{q_s}{\theta}[\mathrm{Lactate}]_s - \left(\frac{1}{2}\right) * k_{tce} * [TCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{dce} * [DCE] * [Lactate] - \left(\frac{1}{2}\right) * k_{vc} * [VC] * [Lactate] - k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.20)$$

$$R_{Acetylene}\frac{\partial([Acetylene])}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\left(\frac{\partial[Acetylene]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(v_i[Acetylene]) + \frac{q_s}{\theta}[Acetylene]_s + k_{tcefe} * [TCE] * [Fe(red)] \quad (3.21)$$

$$\frac{\partial([Fe(red)])}{\partial t} = -k_{tcefe} * [TCE] * [Fe(red)] + k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.22)$$

$$R_{Fe(ox)}\frac{\partial([Fe(ox)])}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\left(\frac{\partial[Fe(ox)]}{\partial x_j}\right)\right) - \frac{\partial}{\partial x_i}(v_i[Fe(ox)]) + \frac{q_s}{\theta}[Fe(ox)]_s + k_{tcefe} * [TCE] * [Fe(red)] - k_{feoxlac} * [Fe(ox)] * [Lactate] \quad (3.23)$$

3.3 RT3D Model Setup

The above stated partial differential equations, Equations 3.16 through 3.23 will be solved using RT3D. The user defined code is shown below in Table 3.2 and will represent Equations 3.8 through 3.15 as implemented using operator splitting in RT3D. That is, Equations 3.8 through 3.15 must be given as reaction rate ODEs and thus the retardation factors are moved to the right-hand-side.

Table 3.2. RT3D user defined subroutine implementing Equations 3.8 through 3.15.

```
c
c
c
      SUBROUTINE Rxns(ncomp,nvrxndata,j,i,k,y,dydt,
     &poros,rhob,reta,rc,nlay,nrow,ncol,vrc)
C*Block 1:*****************************************************************
c List of calling arguments
c ncomp - Total number of components
c nvrxndata - Total number of variable reaction parameters to be input via RCT file
c J, I, K - node location (used if reaction parameters are spatially variable)
c y - Concentration value of all component at the node [array variable y(ncomp)]
c dydt - Computed RHS of your differential equation [array variable dydt(ncomp)]
c poros - porosity of the node
c reta - Retardation factor [ignore dummy reta values of immobile species]
c rhob - bulk density of the node
c rc - Stores spatially constant reaction parameters (can dimension upto 100 values)
c nlay, nrow, ncol - Grid size (used only for dimensioning purposes)
c vrc - Array variable that stores spatially variable reaction parameters

C*End of Block 1************************************************************

C*Block 2:*****************************************************************
C* *Please do not modify this standard interface block*
      !MS$ATTRIBUTES DLLEXPORT :: rxns
      IMPLICIT NONE
      INTEGER ncol,nrow,nlay
      INTEGER ncomp,nvrxndata,j,i,k
      INTEGER, SAVE :: First_time=1
      DOUBLE PRECISION y,dydt,poros,rhob,reta
      DOUBLE PRECISION rc,vrc
      DIMENSION y(ncomp),dydt(ncomp),rc(100)
      DIMENSION vrc(ncol,nrow,nlay,nvrxndata),reta(ncomp)
C*End of block 2************************************************************

C*Block 3:*****************************************************************
c *Declare your problem-specific new variables here*
      DOUBLE PRECISION tce,dce,vc,ethene,acet,lactate,fered,feox
      DOUBLE PRECISION ktce,kdce,kvc,ktcefe,kfeoxlac
C*End of block 3************************************************************

C*Block 4:*****************************************************************
C*Initialize reaction parameters here, if required*
       IF (First_time .EQ. 1) THEN
          First_time = 0 !reset First_time to skip this block later
       END IF
```

Table 3.2 (cont.). RT3D user defined subroutine implementing Equations 3.8 through 3.15.

```
C*End of block 4************************************************************

C*Block 5:******************************************************************
C*Assign or compute the values of new variables, if required*
      tce = y(1)
      dce = y(2)
      vc = y(3)
      ethene = y(4)
      lactate = y(5)
      acet = y(6)
      fered = y(7)
      feox = y(8)
!      ktce = rc(1) ! Use in batch mode
!      kdce = rc(2)
!      kvc = rc(3)
!      ktcefe = rc(4)
!      kfeoxlac = rc(5)
      ktce = vrc(j,i,k,1) ! Use in GMS model to spatilly vary constants
      kdce = vrc(j,i,k,2)
      kvc = vrc(j,i,k,3)
      ktcefe = vrc(j,i,k,4)
      kfeoxlac = vrc(j,i,k,5)
C*End of block 5************************************************************

C*Block 6:******************************************************************
C*Differential Reaction Equations*
      dydt(1) = (- ktce*tce*(lactate)-ktcefe*tce*(fered))/reta(1)
      dydt(2) = (- kdce*dce*(lactate) + ktce*tce*(lactate))/reta(2)
      dydt(3) = (- kvc*vc*(lactate) + kdce*dce*(lactate))/reta(3)
      dydt(4) = (kvc*vc*(lactate))/reta(4)
      dydt(5) = (-0.5*ktce*tce*(lactate) -0.5*kdce*dce*(lactate)
     &          -0.5*kvc*vc*(lactate)-kfeoxlac*feox*(lactate))/reta(5)
      dydt(6) = (ktcefe*tce*(fered))/reta(6)
      dydt(7) = (-ktcefe*tce*(fered) + kfeoxlac*feox*(lactate))/reta(7)
      dydt(8) = (ktcefe*tce*(fered)-kfeoxlac*feox*(lactate))/reta(8)
C*End of block 6************************************************************
      RETURN
      END
```

The code above differs from the one described in Chapter 2 in only three blocks. Block 3 declares a larger number of parameters and variables than the one in Chapter 2. Block 5 similarly contains more variables and rate constants. Similar to Chapter 2 the vrc rate constant should only be used when modeling the entire domain in GMS; the ones with rc can be used in batch mode by uncommenting the lines with those rate constants and commenting the lines with the vrc ones. The code can be recompiled using instructions provided in Appendix A. Lastly, block 6 contains all the rate laws, described in Section 3.2, in the operator split form. The reta is the retardation value calculated in the main RT3D program, and is equal to one in the batch mode.

3.4 Model Verification and Testing in batch mode

This section will present tests to verify model mass balance, using batch mode, for the abiotic processes only. The biotic processes have been shown to meet mass balance in Chapter 2. Additionally, more detailed explanations of batch mode are provided in Chapter 2.

Two scenarios will be tested to verify the abiotic model. Scenario 1 is adding 10 moles/liter (mol/l) for TCE and Fe(red), with all other species at 0 moles/liter; Scenario 2 is adding 10 moles/liter of lactate and Fe(ox), with all others set to 0 moles/liter. The first scenario will test the formation of acetylene by degrading TCE, mass balance will be met if sum total of Fe(red) and Fe(ox) is 10 mol/l and if the total of TCE and acetylene is 10 mol/l. In the second scenario mass balance is met if the concentration of lactate and Fe(red) will add up to be 10 mol/l and if the concentration of Fe(red) and Fe(ox) will add up to be 10 mol/l. The rate constants, ktce, kdce, kvc, ktcefe, and kfeoxlac, are chosen arbitrarily to be 0.005 liter/(mol*day), 0.004 liter/(mol*day), 0.003 liter/(mol*day), 0.002 liter/(mol*day), 0.001 liter/(mol*day), respectively. For both scenarios, ncomp is 8, no_of_timesteps is 10, and time step size, delt, is 1 day. For scenario 1, the initial values are in the following order: 10,0,0,0,0,0,10,0. For scenario 2, the

initial values are in the following order: 0,0,0,0,10,0,0,10. The default tolerance values in RT3D are kept, and lastly, the number of constant reaction parameters is 5, values of which are listed above. An instruction sheet for running RT3D batch mode is provided in Appendix C. The provided instruction sheet is for scenario 1 in Chapter 2. Results for both scenarios are shown below in Figure 3.1 and Figure 3.2, respectively. The mass balance checks are in Tables 3.3 & 3.4.

Mass balance was met for all scenarios, giving us confidence in the RT3D batch mode. In scenario 1, Table 3.3 indicates that the sum of TCE and acetylene sums to the initial input concertation of TCE and that the Fe(red) ad Fe(ox) sums to be initial concentration of Fe(red). Similarly, mass balance is met for scenario 2, where the sum of Fe(red) and Fe(ox) adds to be the input concentration of Fe(ox), shown in Table 3.4. Additionally, in scenario 2, the sum of lactate and Fe(red) adds to be the sum of initial lactate present

Time	TCE	DCE	VC	Ethene	Lactate	Acetylene	Fe(red)	Fe(ox)
0.00000E+00	0.10000E+02	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+02	0.00000E+00
0.10000E+01	0.98039E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.19608E+00	0.98039E+01	0.19608E+00
0.20000E+01	0.96154E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.38462E+00	0.96154E+01	0.38462E+00
0.30000E+01	0.94340E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.56604E+00	0.94340E+01	0.56604E+00
0.40000E+01	0.92593E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.74074E+00	0.92593E+01	0.74074E+00
0.50000E+01	0.90909E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.90909E+00	0.90909E+01	0.90909E+00
0.60000E+01	0.89286E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10714E+01	0.89286E+01	0.10714E+01
0.70000E+01	0.87719E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.12281E+01	0.87719E+01	0.12281E+01
0.80000E+01	0.86207E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.13793E+01	0.86207E+01	0.13793E+01
0.90000E+01	0.84746E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.15254E+01	0.84746E+01	0.15254E+01
0.10000E+02	0.83333E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.16667E+01	0.83333E+01	0.16667E+01

Figure 3.1. Batch mode results for scenario 1.

Table 3.3. Mass balance calculation for scenario 1.

Time	TCE + Acetylene (mol/l)	Fe(red) + Fe(ox) (mol/l)
0.00	10.00	10.00
1.00	10.00	10.00
2.00	10.00	10.00
3.00	10.00	10.00
4.00	10.00	10.00

Table 3.3 (cont.). Mass balance calculation for scenario 1.

5.00	10.00	10.00
6.00	10.00	10.00
7.00	10.00	10.00
8.00	10.00	10.00
9.00	10.00	10.00
10.00	10.00	10.00

Time	TCE	DCE	VC	Ethene	Lactate	Acetylene	Fe(red)	Fe(ox)
0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.10000E+02	0.00000E+00	0.00000E+00	0.10000E+02
0.10000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.99010E+01	0.00000E+00	0.99010E-01	0.99010E+01
0.20000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.98039E+01	0.00000E+00	0.19608E+00	0.98039E+01
0.30000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.97087E+01	0.00000E+00	0.29126E+00	0.97087E+01
0.40000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.96154E+01	0.00000E+00	0.38462E+00	0.96154E+01
0.50000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.95238E+01	0.00000E+00	0.47619E+00	0.95238E+01
0.60000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.94340E+01	0.00000E+00	0.56604E+00	0.94340E+01
0.70000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.93458E+01	0.00000E+00	0.65421E+00	0.93458E+01
0.80000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.92593E+01	0.00000E+00	0.74074E+00	0.92593E+01
0.90000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.91743E+01	0.00000E+00	0.82569E+00	0.91743E+01
0.10000E+02	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.90909E+01	0.00000E+00	0.90909E+00	0.90909E+01

Figure 3.2. Batch mode results for scenario 2.

Table 3.4. Mass balance calculation for scenario 2.

Time (days)	**Fe(red) + Fe(ox) (mol/l)**	**Lactate + Fe(red) (mol/l)**
0.00	10.00	10.00
1.00	10.00	10.00
2.00	10.00	10.00
3.00	10.00	10.00
4.00	10.00	10.00
5.00	10.00	10.00
6.00	10.00	10.00
7.00	10.00	10.00
8.00	10.00	10.00
9.00	10.00	10.00
10.00	10.00	10.00

Lastly, a coupled biotic-abiotic scenario will also be tested. This scenario will have the same values for scenarios 1 and 2 entered in batch mode, except initial values are as follows for TCE, DCE, VC, ethene, lactate, acetylene, Fe(red), Fe(ox): 100, 0, 0, 0, 100, 0, 100, 0

respectively. All initial conditions are in mol/l. The results are compared independently with a simple explicit in time solution of the batch mode reaction equations and the mass balance is checked by verifying that the sum of the concentrations of TCE, DCE, VC, ethene and acetylene adds to 100 mol/l for any timestep. The timestep used in the explicit method is 0.001 days and the equations for the explicit method are as follows.

$$[TCE]_{n+1} = \left(-k_{tce} * [TCE]_n * [Lactate]_n - k_{tcefe}[TCE]_n * [Fe(red)]_n\right) * \Delta t + [TCE]_n \tag{3.24}$$

$$[DCE]_{n+1} = (-k_{dce} * [DCE]_n * [Lactate]_n + k_{tce} * [TCE]_n * [Lactate]_n) * \Delta t + [DCE]_n \tag{3.25}$$

$$[VC]_{n+1} = (-k_{vc} * [VC]_n * [Lactate]_n + k_{dce} * [DCE]_n * [Lactate]_n) * \Delta t + [VC]_n \tag{3.26}$$

$$[Ethene]_{n+1} = (k_{vc} * [VC]_n * [Lactate]_n) * \Delta t + [Ethene]_n \tag{3.27}$$

$$[Lactate]_{n+1} = \left(-\left(\frac{1}{2}\right) * k_{tce} * [TCE]_n * [Lactate]_n - \left(\frac{1}{2}\right) * k_{dce} * [DCE]_n * [Lactate]_n - \left(\frac{1}{2}\right) * k_{vc} * [VC]_n * [Lactate]_n - k_{feoxlac} * [Fe(ox)]_n * [Lactate]_n\right) * \Delta t + [Lactate]_n \tag{3.28}$$

$$[Acetylene]_{n+1} = \left(k_{tcefe} * [TCE]_n * [Fe(red)]_n\right) * \Delta t + [Acetylene]_n \tag{3.29}$$

$$[Fe(red)]_{n+1} = \left(-k_{tcefe} * [TCE]_n * [Fe(red)]_n + k_{feoxlac} * [Fe(ox)]_n * [Lactate]_n\right) * \Delta t + [Fe(red)]_n \tag{3.30}$$

$$[Fe(ox)]_{n+1} = \left(k_{tcefe} * [TCE]_n * [Fe(red)]_n - k_{feoxlac} * [Fe(ox)]_n * [Lactate]_n\right) * \Delta t + [Fe(ox)]_n \quad (3.31)$$

In the coupled system scenario, the sum of concentrations of TCE, DCE, VC, ethene and acetylene adds to 100 mol/l, the initial input concentration of TCE, Table 3.5. The results produced in the coupled system using RT3D also match the ones independently calculated using the explicit method, Figure 3.3, thus verifying the model developed in Section 3.3 in batch mode.

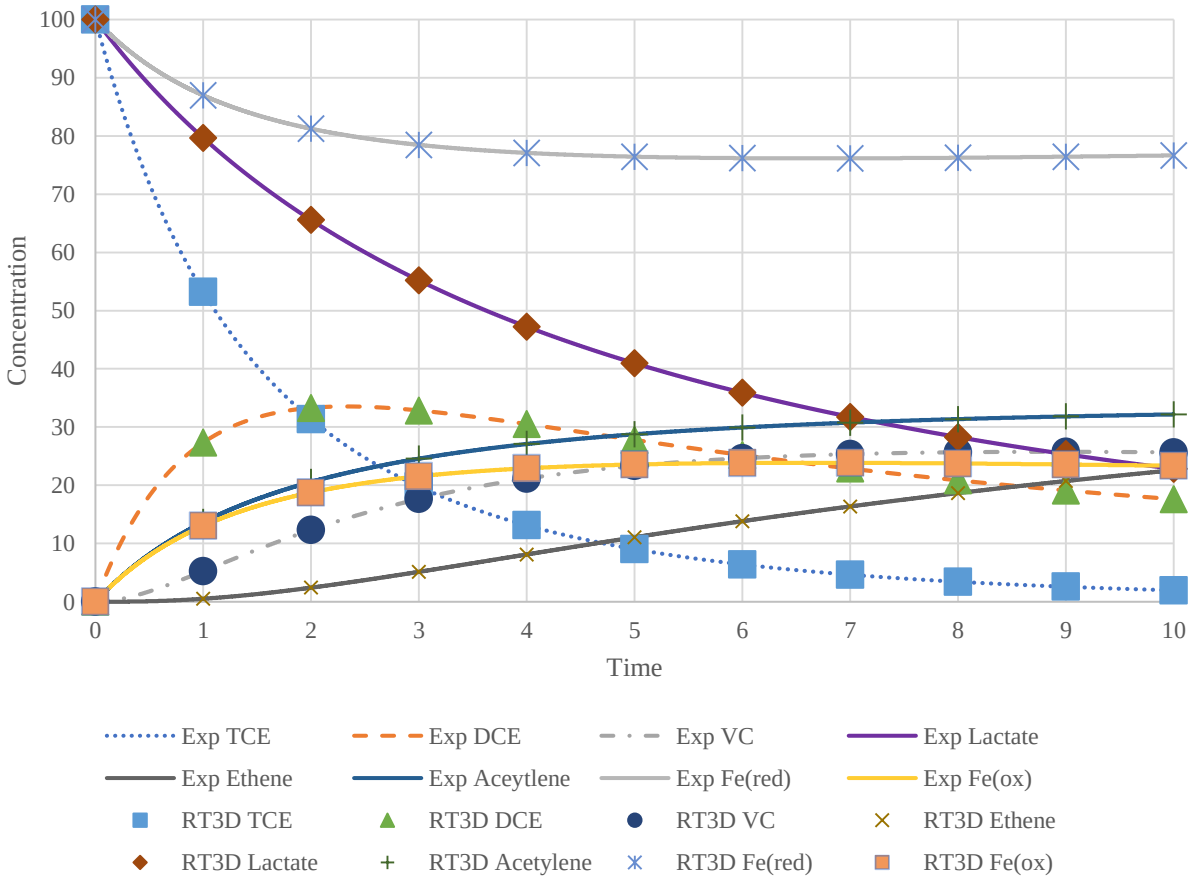

Figure 3.3. RT3D solution in comparison with explicit solution in the coupled system. RT3D calculated concentrations are symbols. Lines are the concentrations computed independently using explicit in time.

Table 3.5. Mass balance verification for the coupled system.

Time	TCE + DCE + VC + Ethene + Acetylene
0.00	100.00
1.00	100.00
2.00	100.00
3.00	100.00
4.00	100.00
5.00	100.00
6.00	100.00
7.00	100.00
8.00	100.00
9.00	100.00
10.00	100.00

3.5 Two-dimensional Model Setup

This section will present the model of the flow cell designed by Erin Berns at University of Texas, Austin. The flow model solved using MODFLOW is the same as the one presented in Chapter 2 Section 6. The RT3D model differs slightly form the one in Chapter 2.6. The number of species used here includes three additional species (acetylene, Fe(red), Fe(ox)), and hence encompasses eight species: TCE (1), DCE (2), VC (3), ethene (4), lactate (5), acetylene (6), Fe(red) (7), and Fe(ox) (8). Table 3.6 summarizes all the parameters and constants used in modeling the flow cell. Another change in the RT3D is that an initial condition containing 0.001 mol/l of Fe(red) is added in the LPZ except for cells containing the TCE constant concentration boundary condition. The initial conditions for all other species are set at zero mol/l. In addition, Fe(red) is treated as an immobile species and as such only the reaction term of the advection-dispersion equation applies. This is done to mimic the presence of Fe(red) in the clay of the experimental flow cell. The immobile treatment of Fe(red), represented in Equation 3.22, is accomplished by assuming it still satisfies the advection-dispersion equation, Equation 2.1, but

that it undergoes linear sorption where the K_d, distribution coefficient is set arbitrarily high at 1E9 in^3/g, in the LPZ and at layer 27, i.e. the HPZ-LPZ interface. The K_d for all other species is set to zero so as to keep those species in the mobile phase. Another minor modification is done to the user defined code, where the reta(7), i.e. the value containing the retardation factor corresponding to Fe(red) is set at 1. This can be done in the user defined subroutine, shown in Table 3.2, by deleting the denominator containing reta(7) in rate law 7 contained in Block 6. This was done so that the decay of Fe(red) is not inhibited by the large K_d and only the fluxes due to advection, diffusion and source/sinks are reduced to zero. The use of immobile species in RT3D was tried without success as the provided RT3D executable crashed anytime an immobile species was present.

Table 3.6. Summary of RT3D model parameters used in the 2D Flow Cell Simulations.

Parameter	Value	Units
Simulation Time Length	100	Day
Diffusion Coefficient	0.04874698	in^2/day
Dispersivity	0	in
HPZ porosity	0.31	Unitless
LPZ porosity	0.06	Unitless
ktce	432	Liter/(mol*day)
kdce	259.2	Liter/(mol*day)
kvc	86.4	Liter/(mol*day)
ktcefe	10	Liter/(mol*day)
kfeoclac	10	Liter/(mol*day)
Bulk density	1600000.0	g/in^3

The diffusion coefficient is the one used to estimate decay in the experimental flow cell (Erin Berns, University of Texas, Austin, Personal Communication, 2016). The dispersivity of zero was chosen because this study only aims to understand the effects of TCE degradation in the LPZ and in the LPZ diffusion dominates. To minimize the impact of numerical dispersion

resulting from the lack of mechanical dispersion, TVD solver, described in Chapter 2 and the MT3DMS user manual, is used (Zheng et al., 1999). The porosity for the HPZ and LPZ was chosen to be similar to the ones estimated in the experimental setup (Erin Berns, University of Texas, Austin, Personal Communication, 2016). The rate constants and the simulation time length were chosen arbitrarily, such that the concentration profile will yield interesting results in a reasonable time frame. Additionally, all rate constants are only activated in the LPZ. Similar to the model in Chapter 2, no sorption is modeled except for the case involving Fe(red). Lastly, the reactions described in the user defined subroutine are solved using a general Gear solver, as detailed in RT3D manual (Clement, 2002). This solver, suitable for stiff problems, will automatically compute the Jacobian using finite-difference approximations.

Boundary conditions for RT3D are shown in Figure 3.4. All boundary conditions are the same as the ones in Chapter 2. The lactate boundary condition, on the left, along the inlet of the HPZ is set at a constant concentration of 0.001 mol/l, while the concentrations for all other species are zero mol/l at this boundary; RT3D doesn't allow users to separately enter a no flux boundary conditions for other species. In addition, the HPZ is surrounded by a no flux boundary at the top of the flow cell. The boundary condition on the right, exit node of the HPZ, is treated as zero gradient boundary; with mass flux equals QC and Q being flow rate, calculated by MODFLOW, and C is concentration at the cell (Zheng et al., 1999). The TCE constant concentration boundary condition at the bottom of the LPZ is set at 0.009 mol/l for TCE, while the other species are zero at this boundary. The LPZ is surrounded by no flux boundaries. The boundary concentration values and locations are chosen to be similar to the ones in the experimental flow cell. The experimental and the simulated flow cell is modeled such that lactate will quickly advect through the HPZ in 5.58 days, as shown in Chapter 2 Section 7, and later

diffuse into the LPZ. In the experimental flow cell, most of the reactions are expected to take place in the LPZ; thus, in the simulated flow cell the rate constants are only specified in the LPZ so that the reactions will only occur in the LPZ.

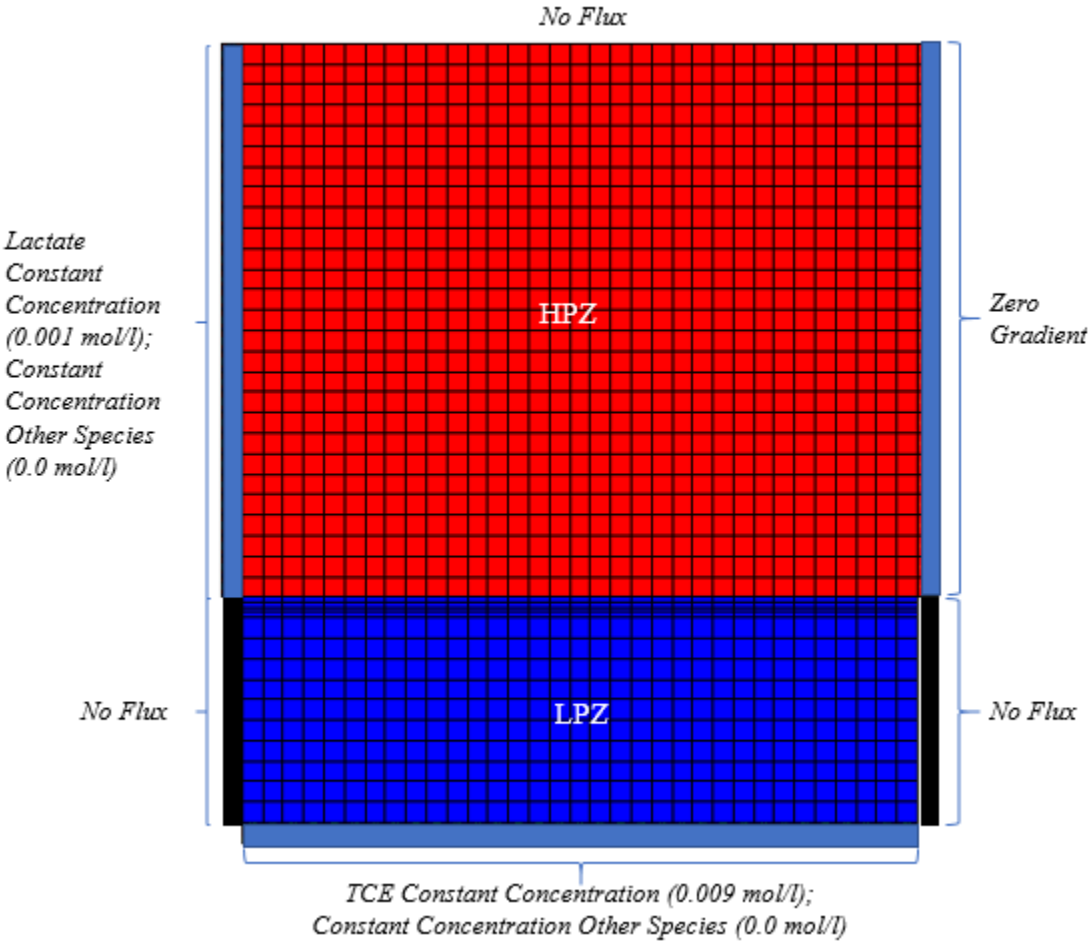

Figure 3.4. Boundary Conditions used in RT3D for the 2D simulations of the combined biotic and abiotic reaction system.

Detailed instructions for the RT3D model setup using GMS are provided in Appendix B Section 3. The flow cell is simulated using GMS version 10.2, a description of which is provided in Chapter 2.

3.6 Two-Dimensional Model Results and Discussion

The concentration profiles are presented for each of the 8 species at 25 days, 75 days and 100 days. The order of the species and figures is as follows: TCE (1), DCE (2), VC (3), ethene (4), lactate (5), acetylene (6), Fe(red) (7), and Fe(ox) (8). The timestep used in this simulation was 0.1539024 days. This timestep was automatically calculated by RT3D to satisfy stability conditions; see the details in the MT3DMS manual (Zheng et al., 1999). Additionally, concentration profiles without any reactions were also calculated and are shown for TCE, lactate and Fe(red). The concentration profiles without decay, i.e. without reactions, are calculated by making all the rate constants 0.0 Liter/(mol*day).

Figures 3.5 through 3.7 show that the TCE continued to diffuse upwards as TCE decayed. This is especially seen in Figures 3.7 and 3.8 where concentration profiles are presented at 100 days with rate constants which allow for decay of TCE, Figure 3.7, and with rate constants where no decay occurred, Figure 3.8. In the decay case, TCE travelled a smaller distance along the LPZ as compared with the no decay case. For the decay case TCE was consumed to directly produce DCE and acetylene, production of which is seen in the later figures.

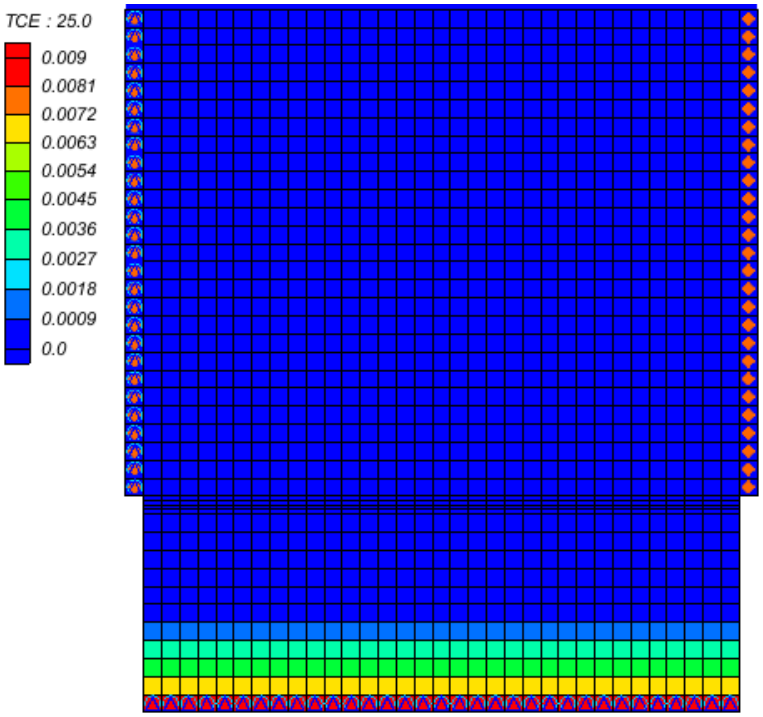

Figure 3.5. TCE concentration profile at 25 days; all concentrations are in moles/liter.

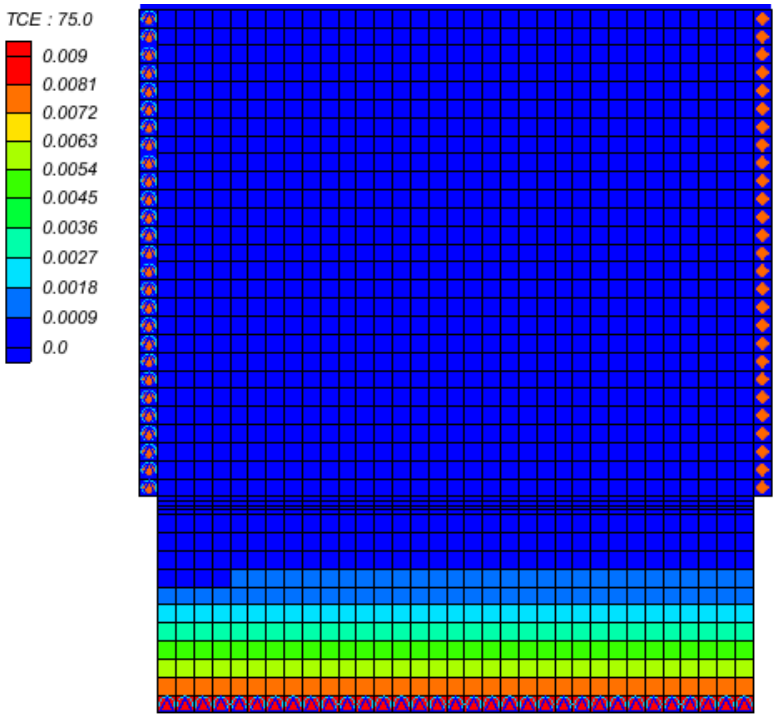

Figure 3.6.TCE concentration profile at 75 days; all concentrations are in moles/liter.

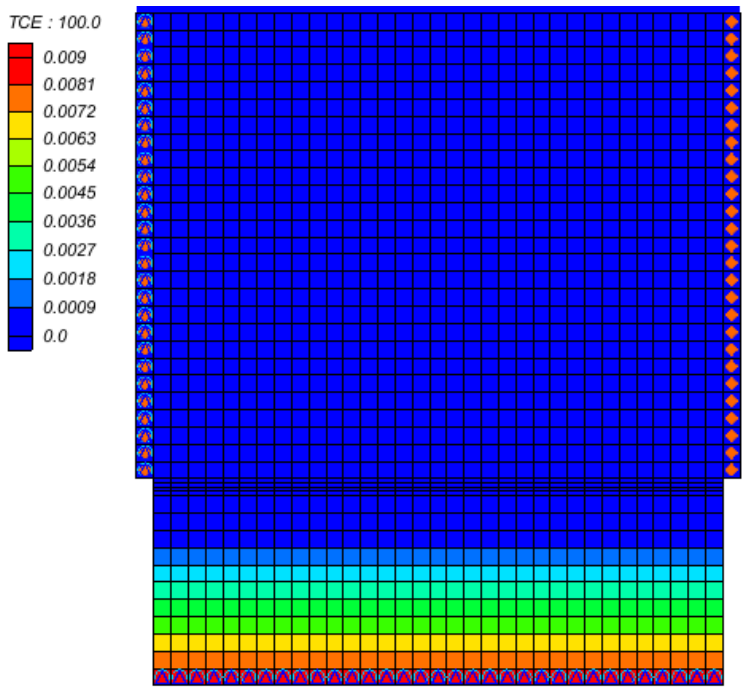

Figure 3.7.TCE concentration profile at 100 days; all concentrations are in moles/liter.

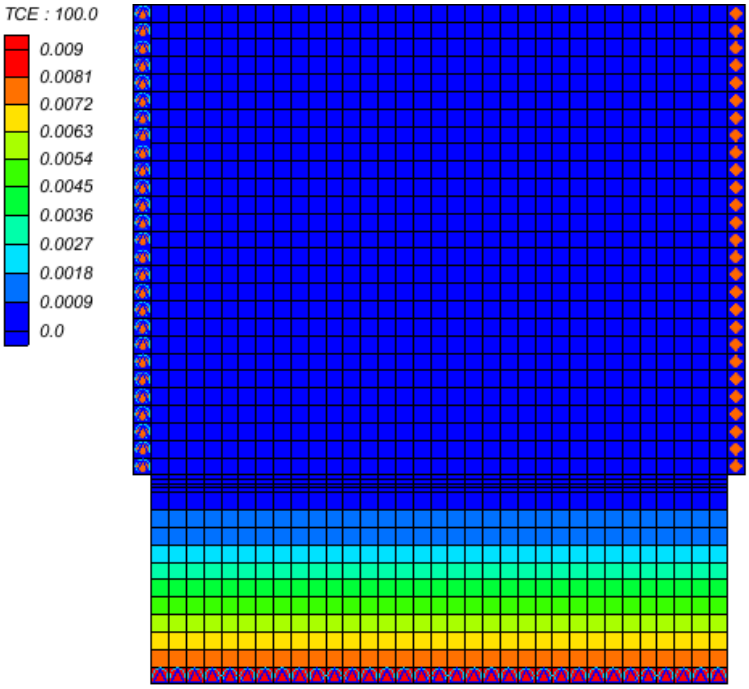

Figure 3.8. TCE concentration profile with no decay at 100 days; all concentrations are in moles/liter.

The formation of the products of TCE degradation is clearly demonstrated: DCE (Figures 3.9-3.11); VC (Figures 3.12-3.14); Ethene (Figures 3.15-3.17). The figures also indicated than an insignificant amount of VC and Ethene was present at day 25, Figures 3.12 and 3.15 respectively. The peak concentration value for VC was smaller than that of DCE and the peak concentration value for ethene was smaller than for VC. Thus, corroborating the sequential nature of decay of DCE to VC to ethene.

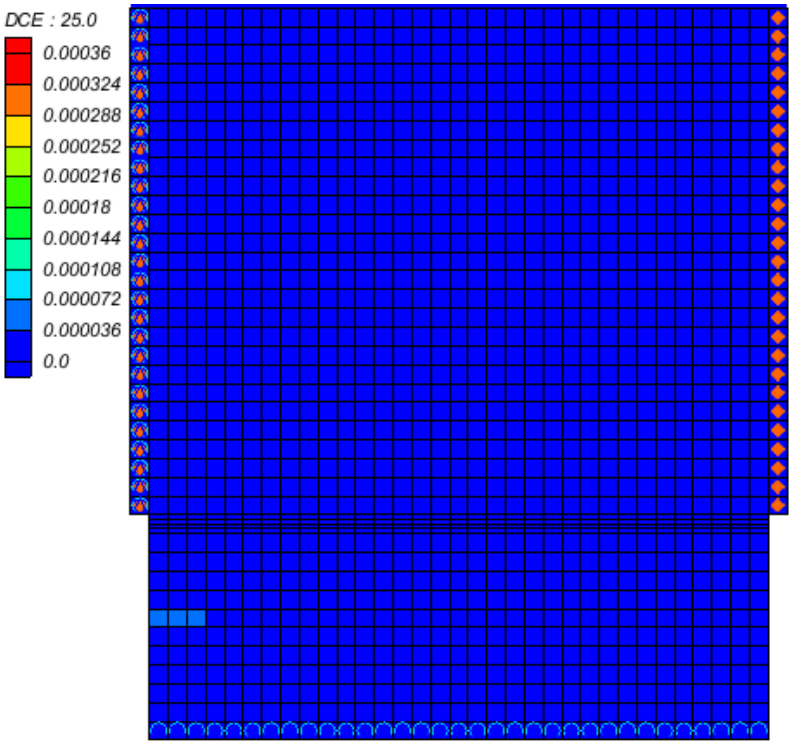

Figure 3.9. DCE concentration profile at 25 days; all concentrations are in moles/liter.

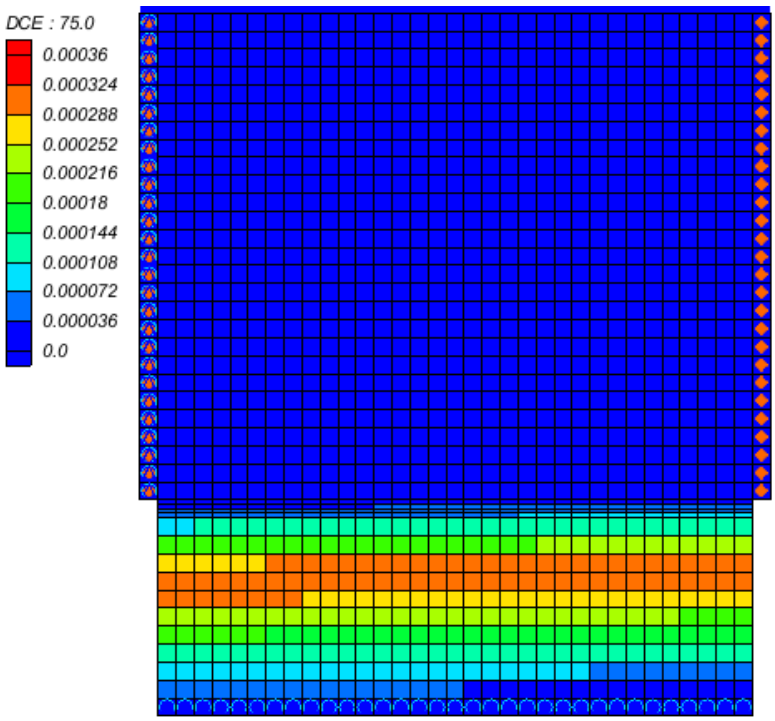

Figure 3.10. DCE concentration profile at 75 days; all concentrations are in moles/liter.

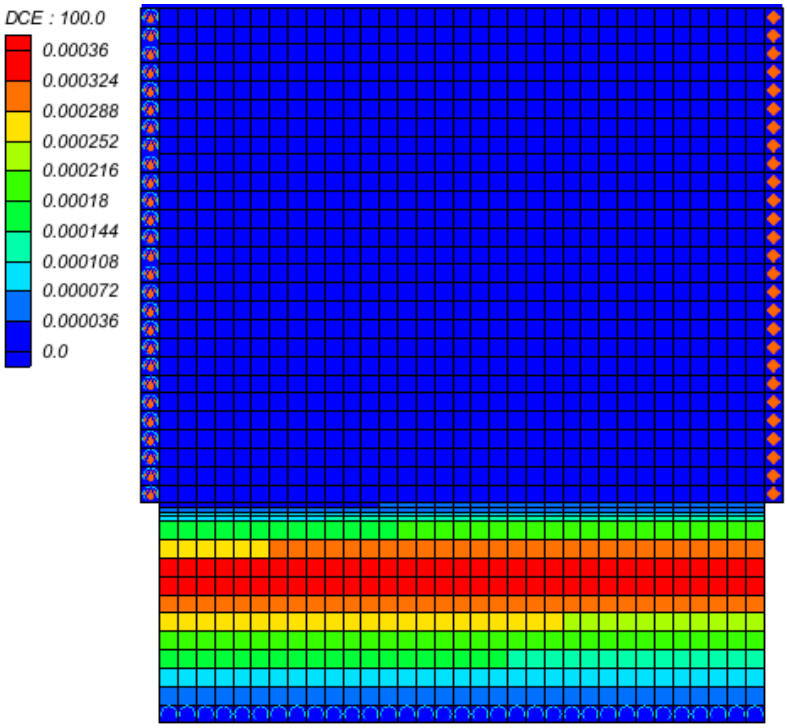

Figure 3.11. DCE concentration profile at 100 days; all concentrations are in moles/liter.

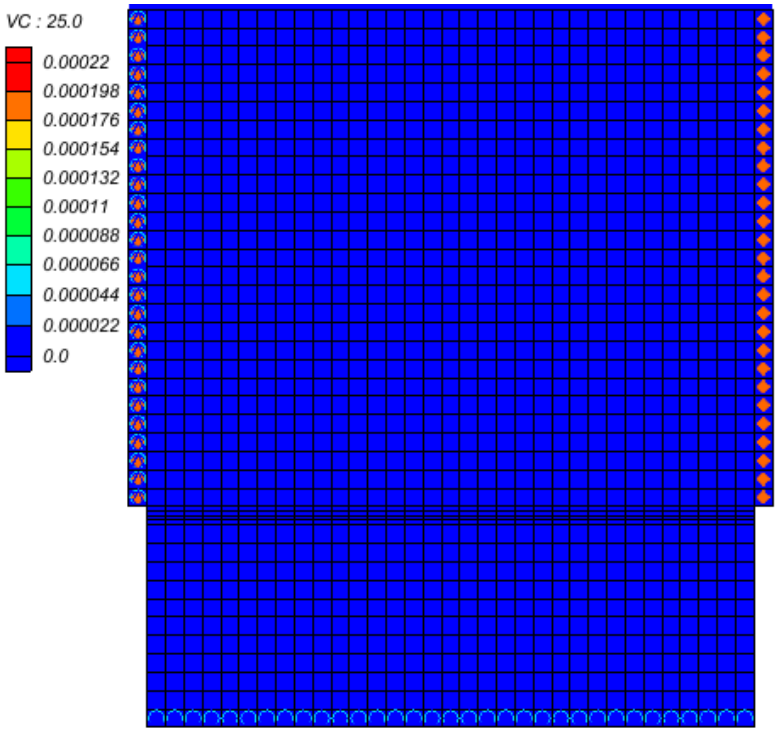

Figure 3.12. VC concentration profile at 25 days; all concentrations are in moles/liter.

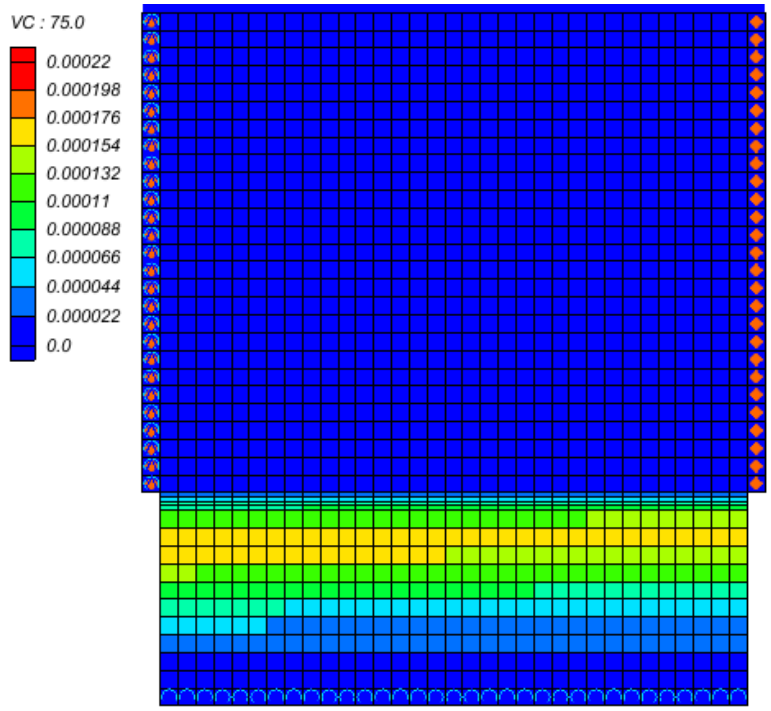

Figure 3.13. VC concentration profile at 75 days; all concentrations are in moles/liter.

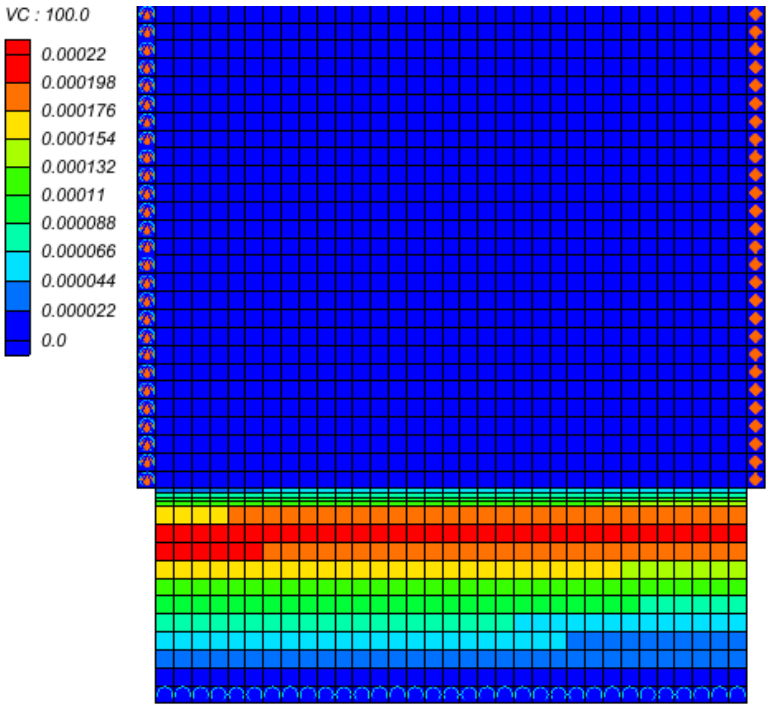

Figure 3.14. VC concentration profile at 100 days; all concentrations are in moles/liter.

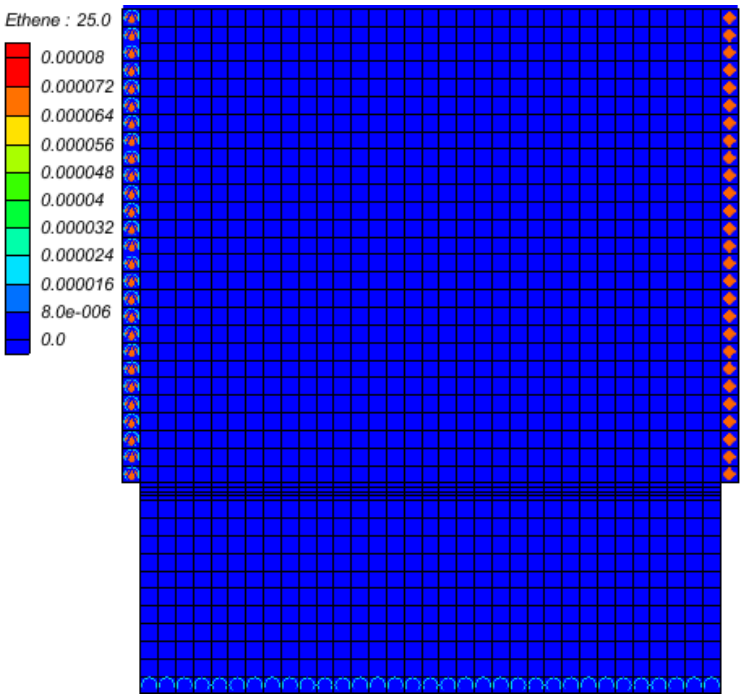

Figure 3.15. Ethene concentration profile at 25 days; all concentrations are in moles/liter.

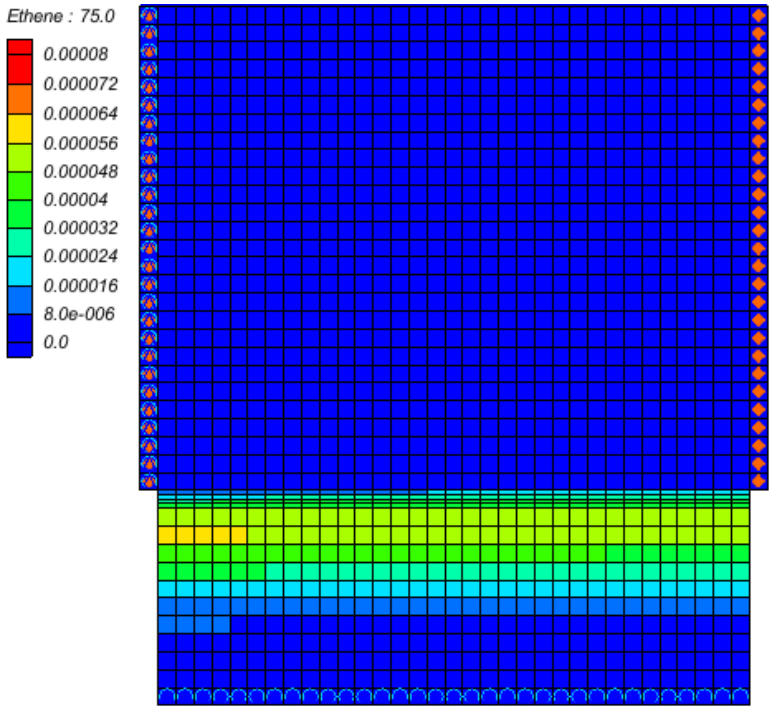

Figure 3.16. Ethene concentration profile at 75 days; all concentrations are in moles/liter.

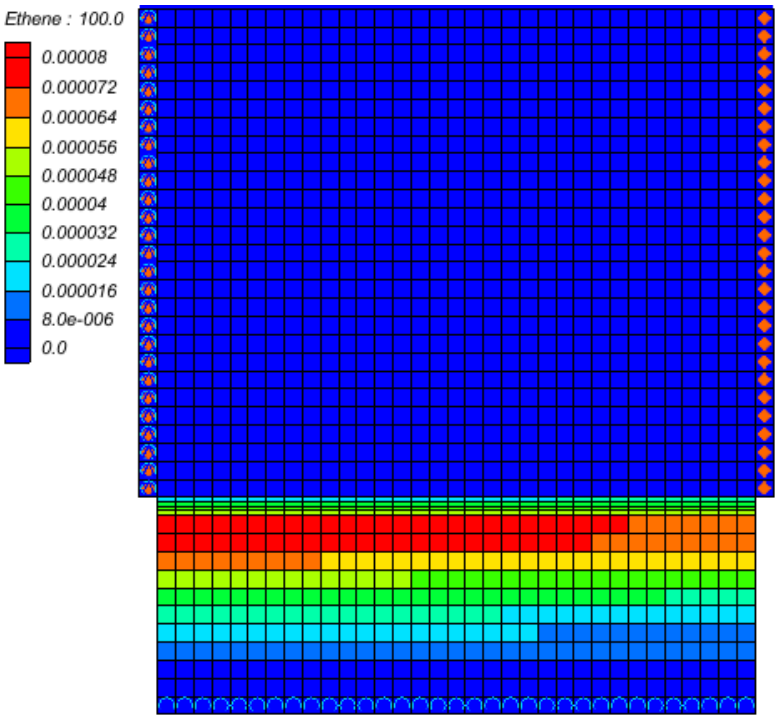

Figure 3.17. Ethene concentration profile at 100 days; all concentrations are in moles/liter.

Lactate diffused into the LPZ, as expected, as seen in Figures 3.18 through 3.20. Lactate was also consumed over time, as seen by noting that the penetration depth of the concentration profile in Figures 3.19 and 3.20 at days 75 and 100 day, respectively, is less than that at day 25, shown in Figure 3.18. This also seen when comparing decay at 100 days, Figure 3.20, with the no decay setup at 100 days, Figure 3.21; with decay, lactate did not diffuse into the LPZ as deep as the case with no decay.

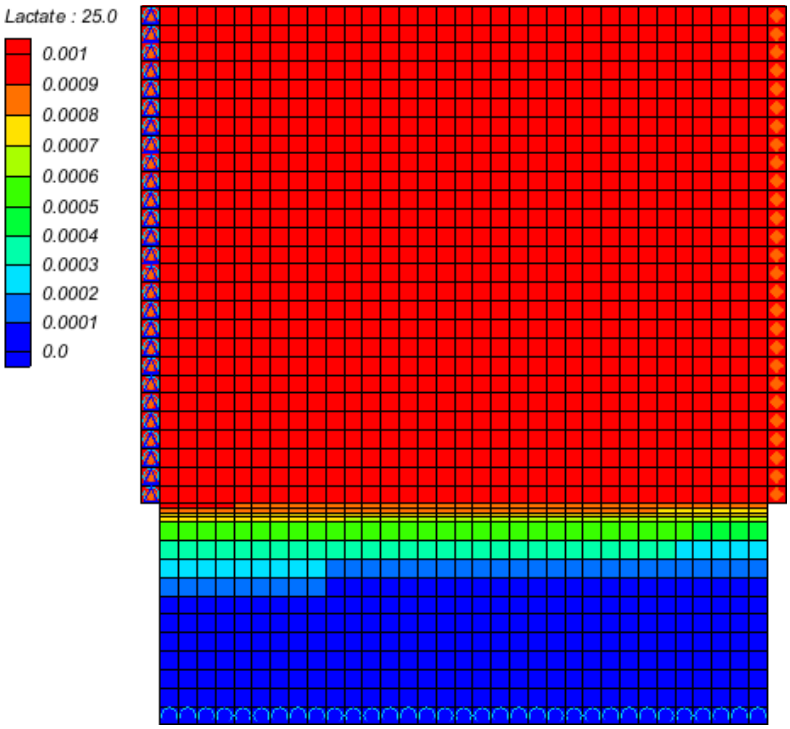

Figure 3.18. Lactate concentration profile at 25 days; all concentrations are in moles/liter.

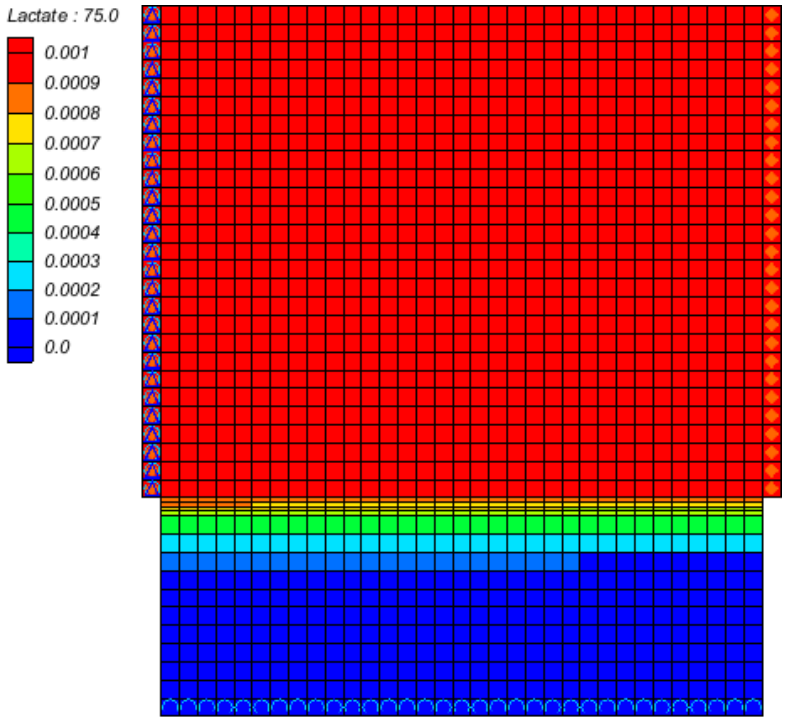

Figure 3.19. Lactate concentration profile at 75 days; all concentrations are in moles/liter.

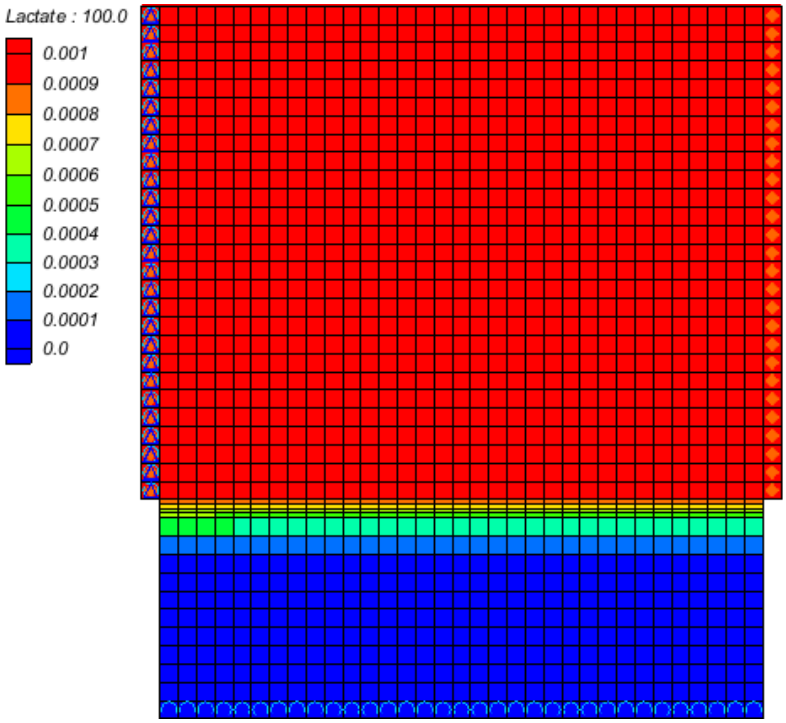

Figure 3.20. Lactate concentration profile at 100 days; all concentrations are in moles/liter.

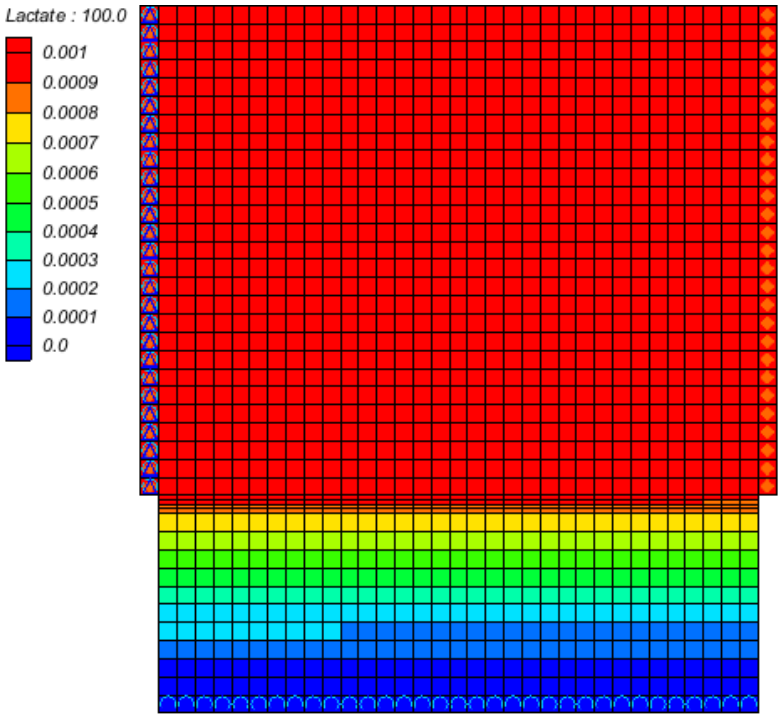

Figure 3.21. Lactate concentration profile at 100 days with no decay; all concentrations are in moles/liter.

Figures 3.22 and 3.25 show the acetylene and Fe(red) at time 25 days and demonstrate the effect of reaction described in Equation 3.13, i.e., that acetylene is produced from the reaction of TCE with Fe(red). The concentration profiles for acetylene, Figure 3.22, and Fe(ox), Figure 3.29, are the same at day 25 because both are equi-molar products of the TCE reaction, Equations 3.13 and 3.15, and an insignificant amount of lactate is present to react with Fe(ox). Despite this Figures 3.23 and 3.24 for acetylene, and Figures 3.30 and 3.31 for Fe(ox) show slightly different concentration profiles at day 75 and 100, respectively. These figures also indicate that acetylene formation is a bit greater than that of Fe(ox). This is because Fe(ox) decayed to form Fe(red) in the presence of lactate and subsequently Fe(red) was used to form acetylene, resulting in a greater formation of acetylene and a smaller amount of Fe(ox). Figures 3.25 through 3.27 also present the decay of Fe(red). This is more significant in the case with

decay in comparison with the case with no decay, as shown in Figures 3.27 and 3.28, respectively.

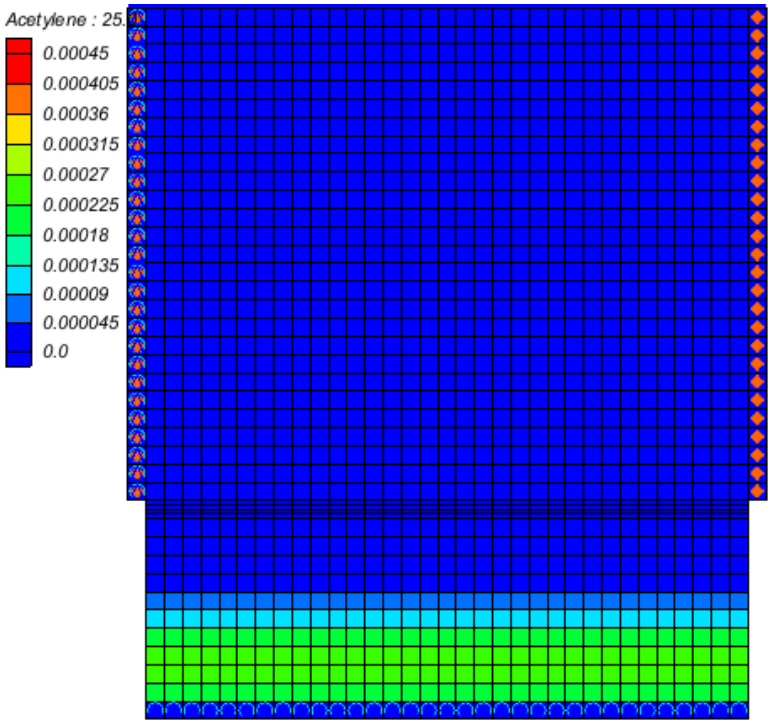

Figure 3.22. Acetylene concertation profile at 25 days; all concentrations are in moles/liter.

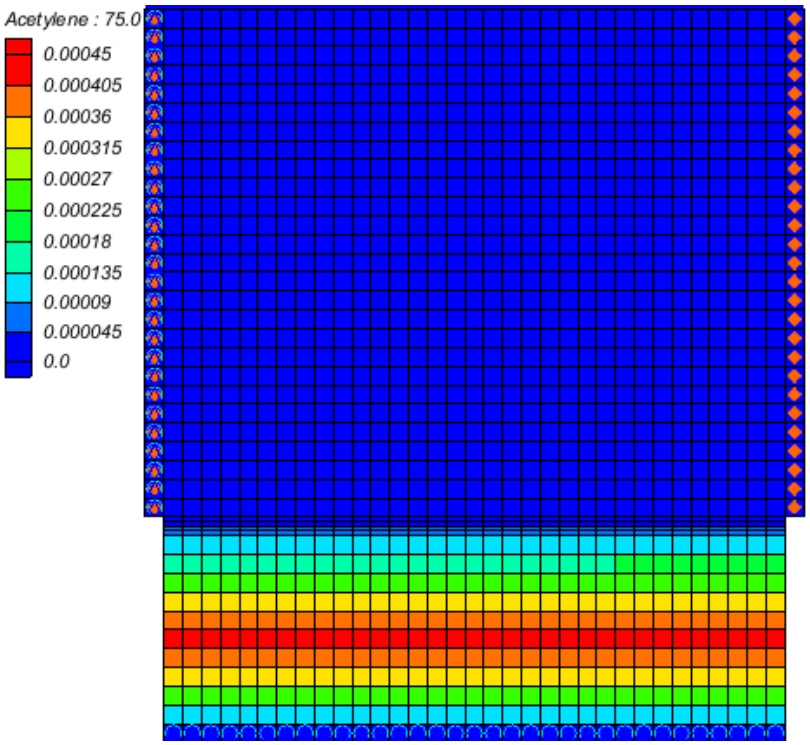

Figure 3.23. Acetylene concentration profile at 75 days; all concentrations are in moles/liter.

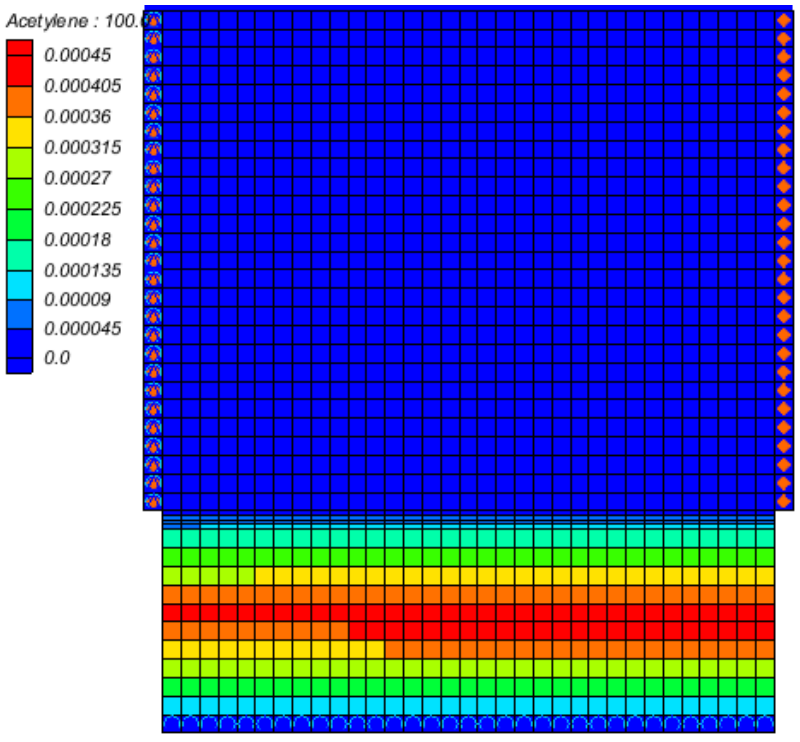

Figure 3.24. Acetylene concentration profile at 100 days; all concentrations are in moles/liter.

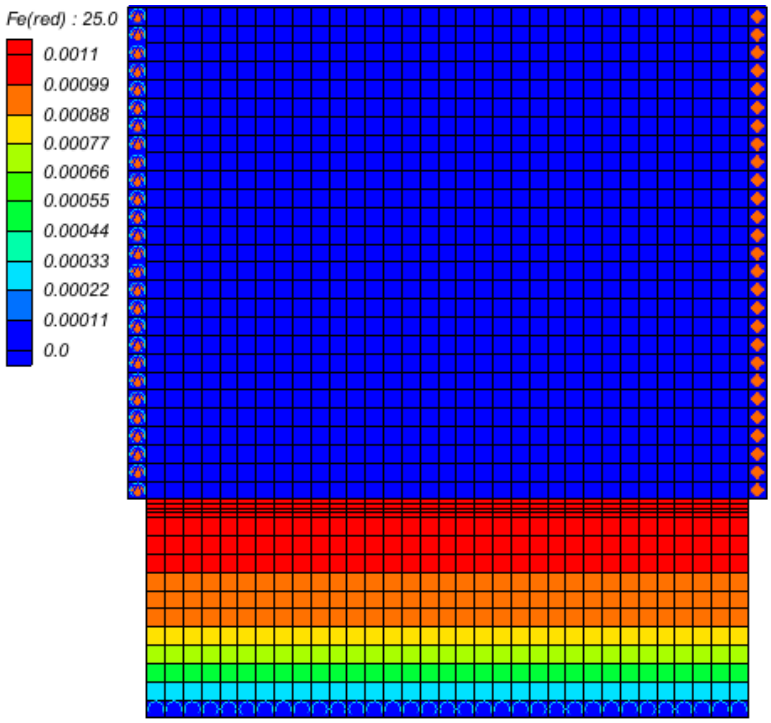

Figure 3.25. Fe(red) concentration profile at 25 days; all concentrations are in moles/liter.

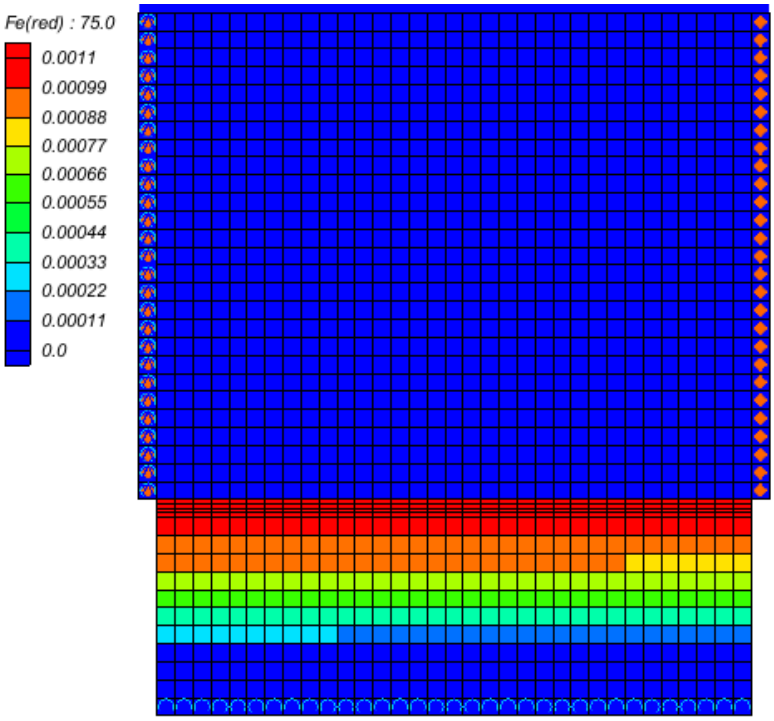

Figure 3.26. Fe(red) concentration profile at 75 days; all concentrations are in moles/liter.

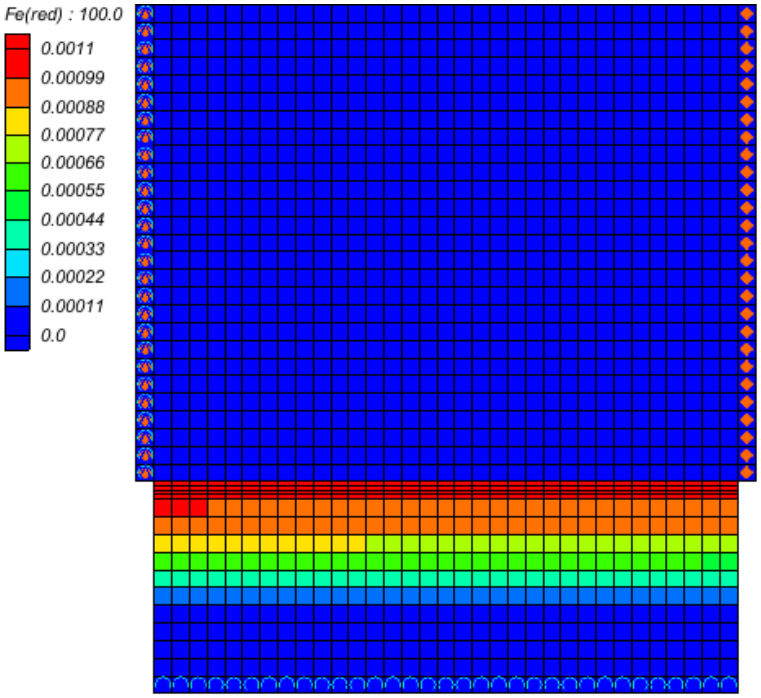

Figure 3.27. Fe(red) concentration profile at 100 days; all concentrations are in moles/liter.

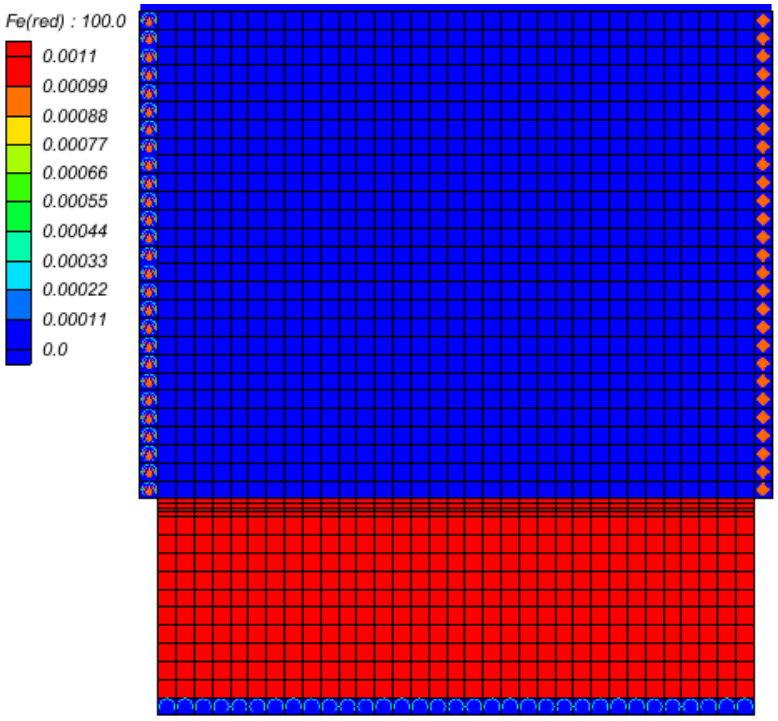

Figure 3.28. Fe(red) concentration profile at 100 days with no decay; all concentrations are in moles/liter.

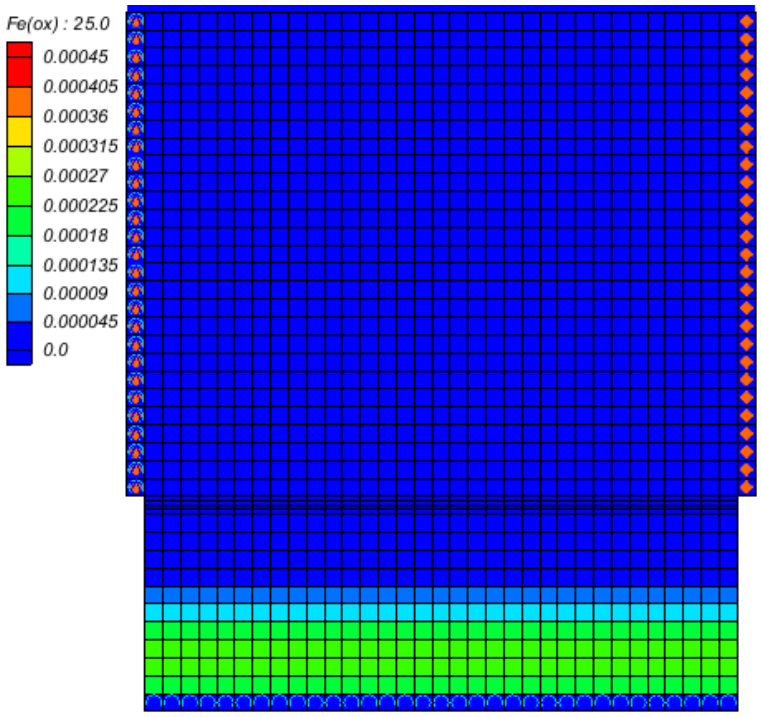

Figure 3.29. Fe(ox) concentration profile at 25 days; all concentrations are in moles/liter.

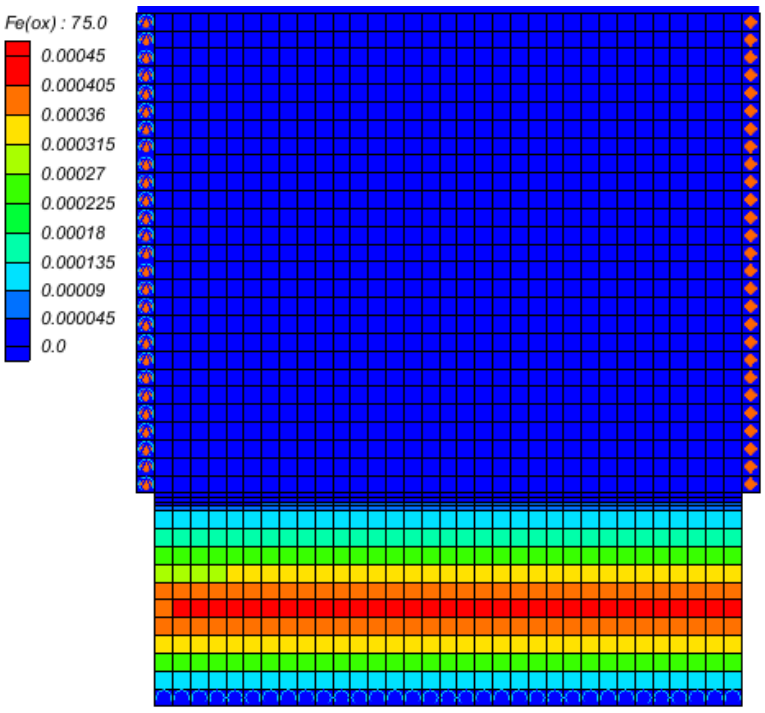

Figure 3.30. Fe(ox) concentration profile at 75 days; all concentrations are in moles/liter.

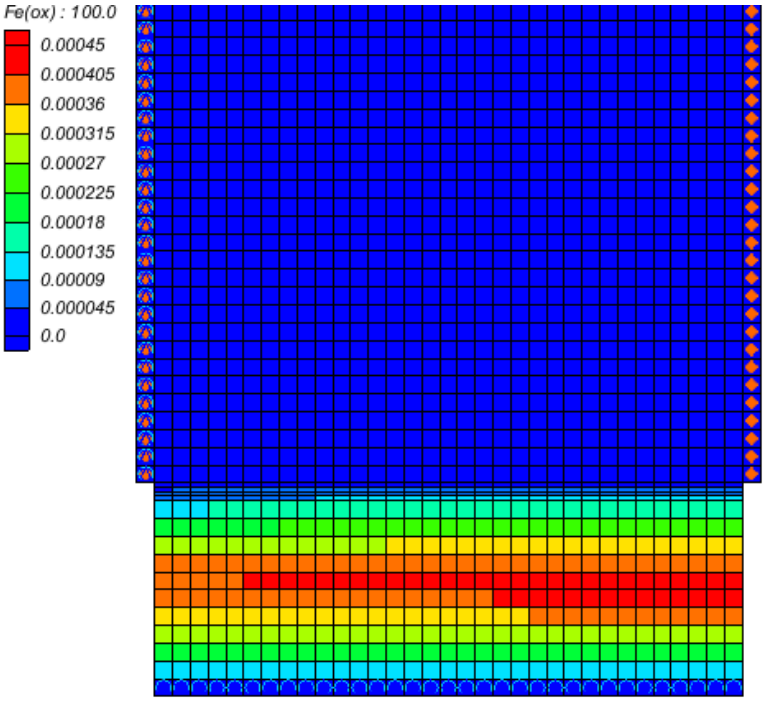

Figure 3.31. Fe(ox) concentration profile at 100 days; all concentrations are in moles/liter.

Several concentration profiles plotted for the middle column of the LPZ, i.e. column 17 of layers 28 through 42. Figure 3.37 shows the locations where the concentration profiles are calculated.

Figure 3.32 accurately shows that no species were formed at the first time step and that no lactate is present initially; lactate is expected to have advected roughly 0.5 inch out of the total 17.5 in flow cell at the first time step. Figure 3.33 indicated limited decay of Fe(red) at day 25. Figure 3.33 also shows that the same amounts of acetylene and Fe(ox) formed because limited amounts of lactate were present to form Fe(red) using Fe(ox). In addition, Figure 3.34 at day 75 indicates the sequential formation of DCE, VC and ethene, with DCE having the highest peak concentration followed by VC and then ethene. Additionally, Figure 3.35 at day 100 presents some variation in the amounts of acetylene and Fe(ox), with acetylene being marginally higher than Fe(ox). This is explained because Fe(ox) is consumed to form Fe(red) which is later

consumed to form acetylene. The results only indicate a minor difference between the concentrations of acetylene and Fe(ox) because only small amounts of lactate were present at the location of Fe(ox) decay. Furthermore, Figures 3.32 through 3.35 show the concentration profile of Fe(red) receding over time, thus highlighting the consumption of Fe(red). Lastly, Figure 3.36 shows an order of magnitude decrease in the amount of TCE present in the HPZ when compared with decay and the no decay case. This showcased the mitigation of the effects back diffusion in situations where the coupled abiotic and biotic reactions are present in the LPZ.

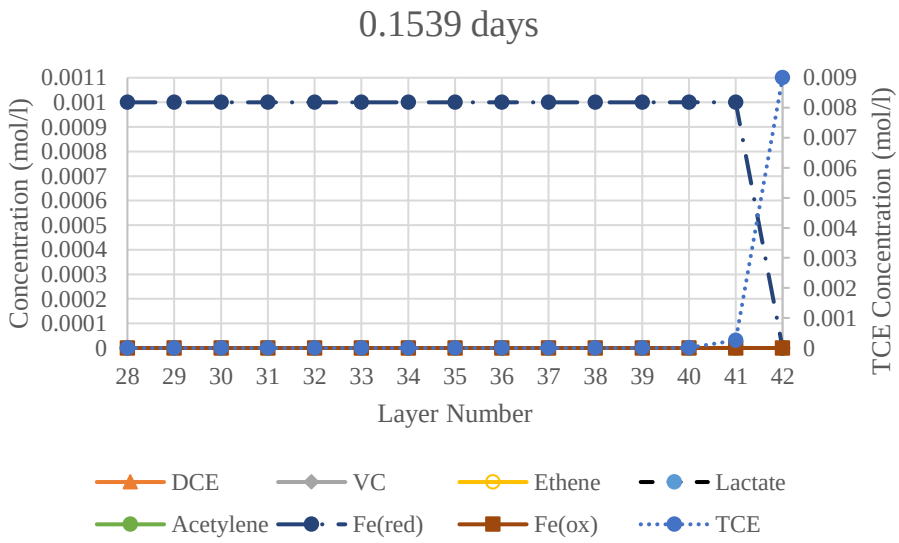

Figure 3.32. Concentration profile across the column 17 of the LPZ (see Fig. 3.37) at 0.1539 days. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

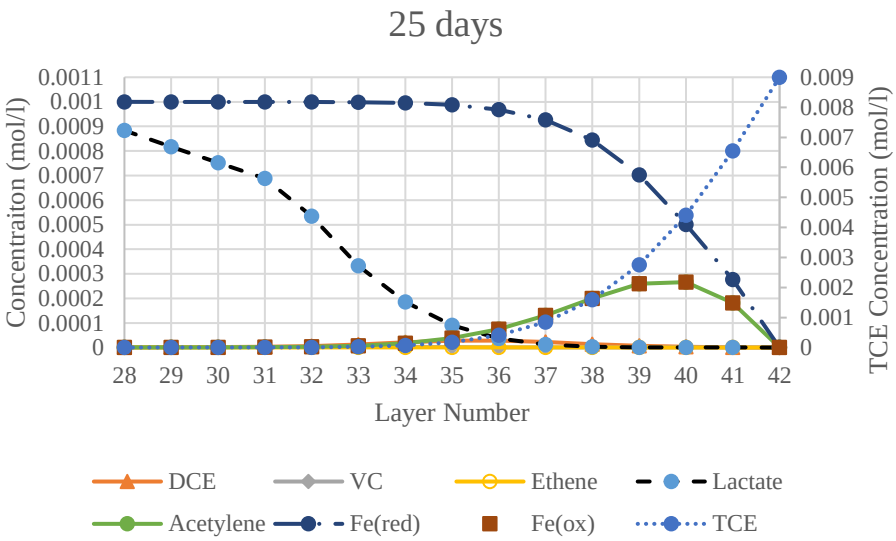

Figure 3.33. Concentration profile across column 17 of the LPZ (see Fig. 3.37) at 25 days. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

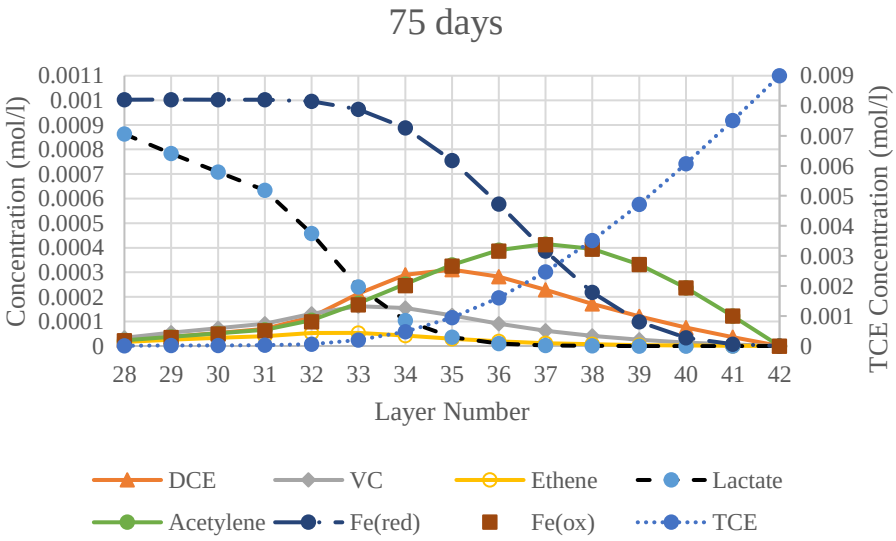

Figure 3.34. Concentration profile across the column 17 of the LPZ (see Fig. 3.37) at 75 days. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

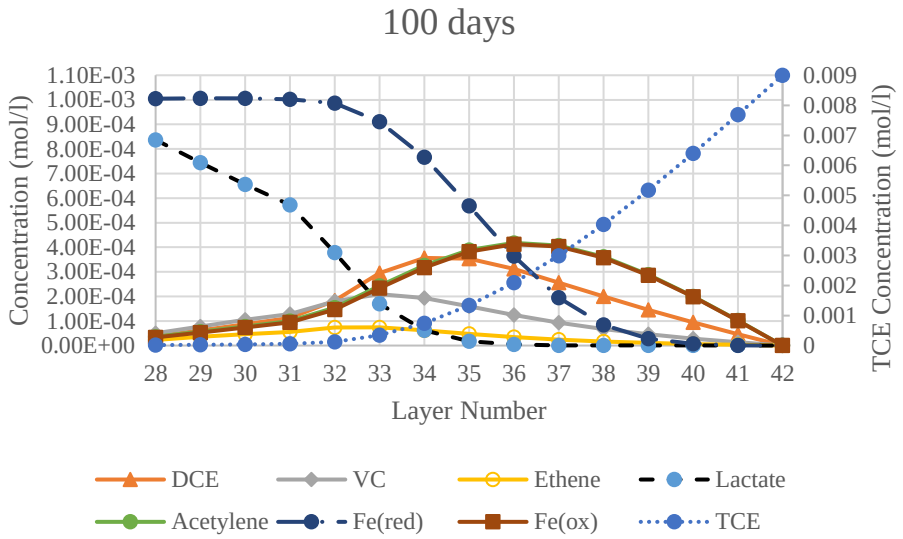

Figure 3.35. Concentration profile across the column 17 of the LPZ (see Fig. 3.37) at 100 days. Axis on the left indicates the concentrations for all species except TCE; axis on the right represents the concentration of TCE.

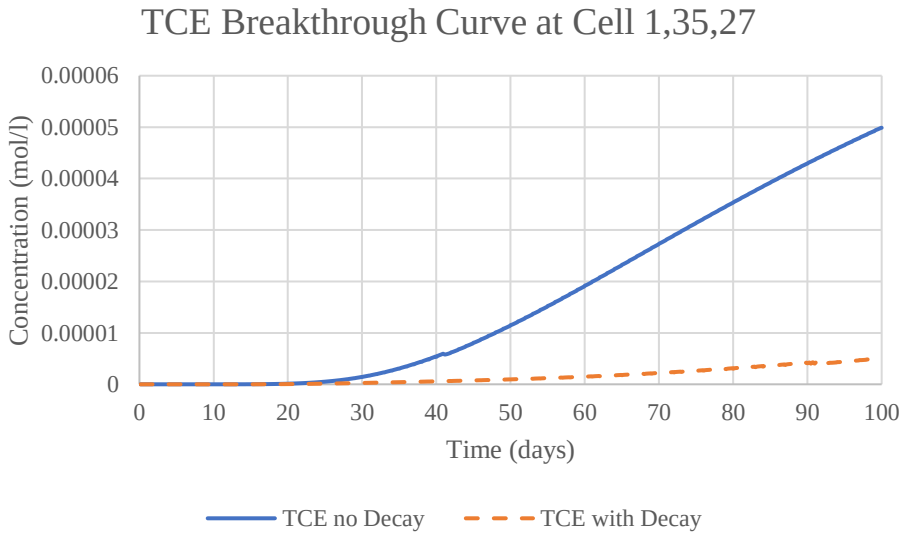

Figure 3.36. TCE breakthrough curve with and without decay at cell 1,35,27. This cell is the exit cell near the HPZ-LPZ interface, shown in Figure 3.37.

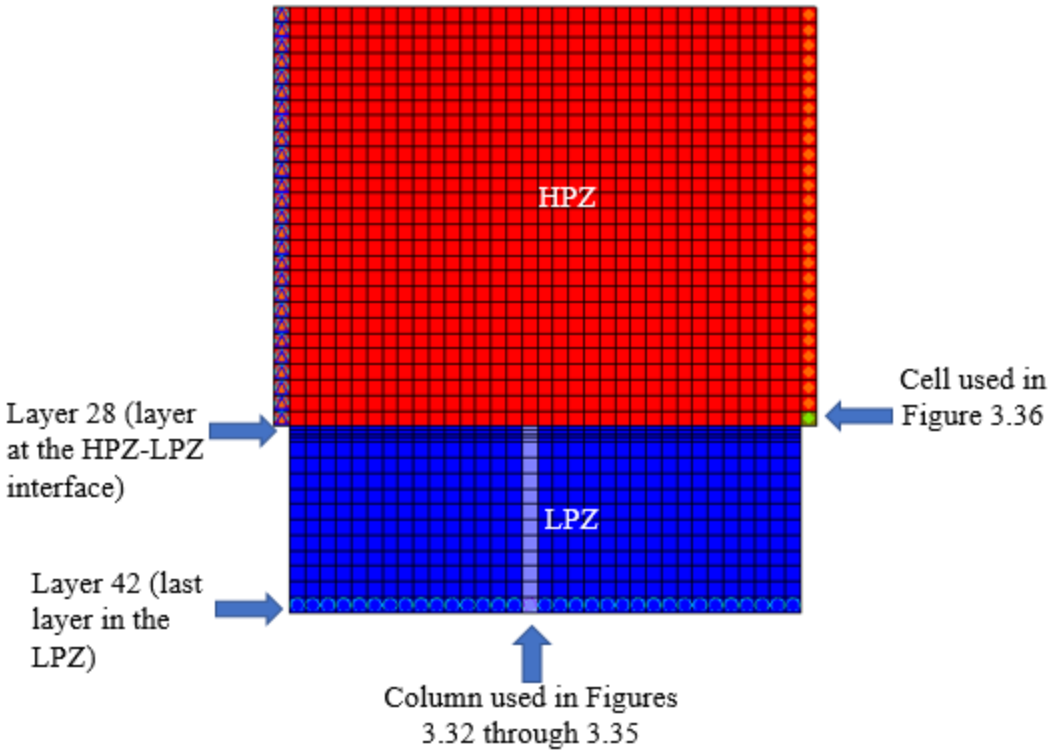

Figure 3.37. Figure indicates the locations in the simulated flow cell used for calculating the concentration profiles in Figures 3.32 through 3.35, colored light blue, and Figure 3.36, colored light green.

3.7 Closing Remarks

In this chapter, we have shown how to model additional abiotic reactions between TCE and reduced iron minerals that have been documented to be potentially important in LPZs. These additional reactions were incorporated into the RT3D code and used to simulate transport and reaction processes in the experimental flow cell developed at UT-Austin. Several assumptions were made in the creation of the coupled abiotic-biotic decay model, the most important of which was the assumption of second order rate behavior. Another important assumption is simplifying the iron species into Fe(red) and Fe(ox), thus ignoring the possibility for speciation. In the case iron chemistry is important, the user should not use this model. It is also important to note that this model should not be used unless the field results indicate the

same chemistry and rate laws as described in Section 3.2. Additionally, this chapter assumed rate constants which may differ from field conditions; prior to usage of this model the user should also estimate the rate constants based on field conditions.

Chapter 4: Conclusion

The thesis goals of modeling the fate and transport of TCE by biotic and abiotic decay reactions were met. A secondary objective to implement these biotic and abiotic reactions in RT3D user defined subroutines was also met. Chapter 2 demonstrates development of a user defined subroutine for the biotic decay reactions. Chapter 2 also verified the results from the user defined subroutine in batch mode and implemented these reactions in a 2-D flow cell. Chapter 3 demonstrates how to implement a coupled abiotic and biotic system, showcasing the competition and interactions between these reactions while transforming TCE.

Chapter 2 presented the model for biotic transformation of TCE into DCE, VC and ethene using lactate as a donor. Results from Chapter 2 showed the sequential formation of DCE to ethene, as expected. However, since the biotic reactions were modeled as second-order, it is possible that the reactions can cease if the supply of electron donor is exhausted. Chapter 3 showed an interesting competition between biotic and abiotic systems with TCE being consumed in both systems. Additionally, the product of the abiotic transformation reaction (Fe(ox)) can react with lactate due to iron reduction reactions to regenerate Fe(red) which is the main reactant in abiotic reduction of TCE. Moreover, the electron donor (lactate) used by the iron reducing bacteria is also used in the biotic reductive dechlorination reaction, thereby presenting a competition for the electron donor.

Implementation of user-defined reactions in RT3D proved challenging due to legacy code issues and incompatibility with modern compilers. We were able to address the challenges in communication between the provided RT3D executable and the user defined dll. These challenges were resolved using techniques detailed in Appendix A.

Although the models developed in this thesis described the fate and transport of TCE, these models should only be used if field conditions support the model chemistry described in Sections 2.2, 3.1 and 3.2. Additionally, the user should determine whether the assumptions used in these models are applicable to the field site. Lastly, the user should determine proper rate constants needed to implement these models.

No model is truly ever complete. Future work can include adding more kinetic reactions that further resemble the system chemistry. This thesis also successfully demonstrated the process of implementing any arbitrary user-defined reaction module into RT3D. Therefore, future users will be able to use RT3D if new knowledge allows for improvements and modifications to the reactions presented in this thesis. If iron mineral speciation and other geochemical processes prove important to capture abiotic reactions, RT3D may not be the best model and it is advised to explore use of a different MODFLOW based package, such as PHT3D.

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Appendix A. How to compile user-defined reaction subroutine in RT3D to link to the RT3D executable provided by GMS version 10.2?

For this thesis, two options were tried to run RT3D. In the end option two proved successful in implementing the RT3D user defined option. The two options tried were:

1. Compile the entire of RT3D using the RT3D source code in a single RT3D executable, instructions in RT3D manual (Clement, 1997, 2002).
    a. This caused issues when this newly compiled RT3D tried to communicate with flow transport link file provided by the MODFLOW simulation.
2. Compile a dynamic link library, dll, containing the user defined subroutine and then linking this subroutine to the GMS provided RT3D executable.
    a. Several problems were found when trying to communicate between the GMS provided RT3D executable but these issues were successfully resolved.

This appendix will provide instructions on properly compiling the dll file so that the file will communicate with the GMS provided RT3D executable.

Note: The instructions below are using Intel® Visual Fortran 2013 Initial Release and Microsoft Visual Studio 2010. The instructions below assume that the user has already installed a version of Intel® Visual Fortran and Microsoft Visual Studio. In addition, these instructions were used on a Windows 8.1 64-bit Operating System. Instructions are provided below:

Additional note: These instructions are provided as-is and the author does not and will not accept any responsibility for consequences of using these instructions including but not limited to damage, data loss or misinterpretation resulting from the use of these instructions or for whether these instructions will serve any particular purpose.

1. Open Microsoft Visual Studio and start a new dynamic link library project.
    a. File > New > Project > Intel® Visual Fortran > Library > Dynamic-link Library > Name: rxns > Location: Pick a location (Figure A.1)

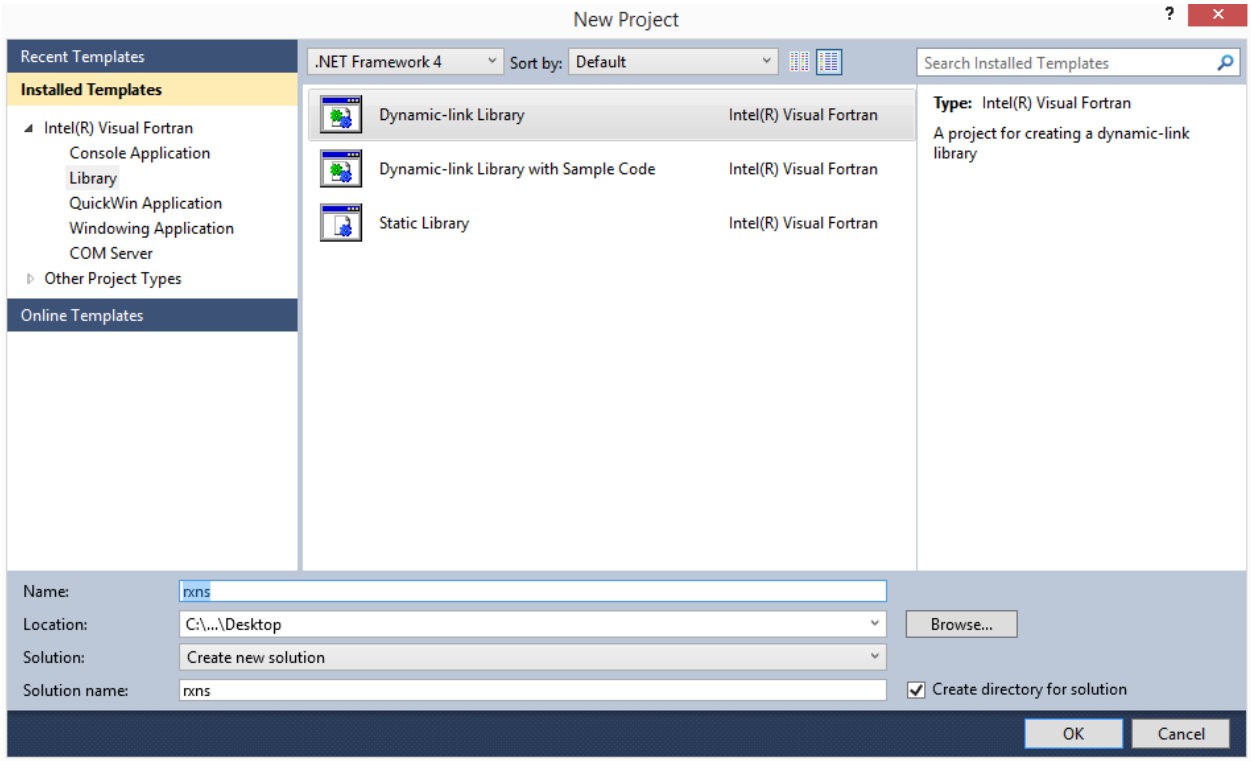


Figure A.1. Displays the new project window in Microsoft Visual Studio 2010 Shell.

2. Click Ok
3. Add the Fortran file containing the user defined subroutine, typically this will be called rxns.f, to the project. A good practice is to place the user defined Fortran file in the same location as the one used for the project.
    a. Project (located in the top toolbar) > Add Existing Item > Select the user defined Fortran subroutine file > Press Ok
        i. The Fortran file will now appear in the solution explorer, see Figure A.2

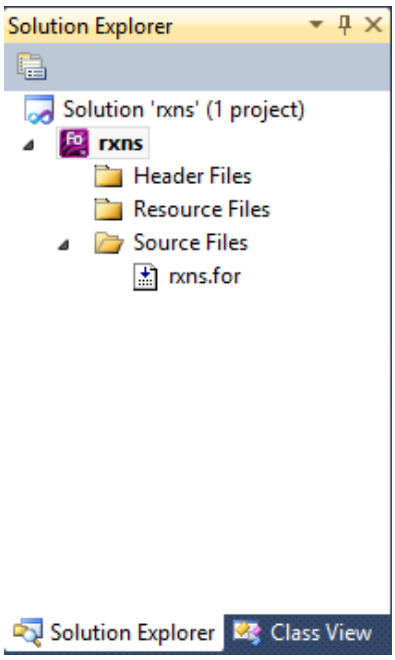


Figure A.2. Solution explorer window in Microsoft Visual Studio 2010 Shell, displaying the user defined rxns.f file.

4. Change the Solution Configuration to Release and the Solution Platform to Win 32.
    a. Build (located in top toolbar) > Configuration Manager > Change the configuration to the following, Figure A.3 > Click Close

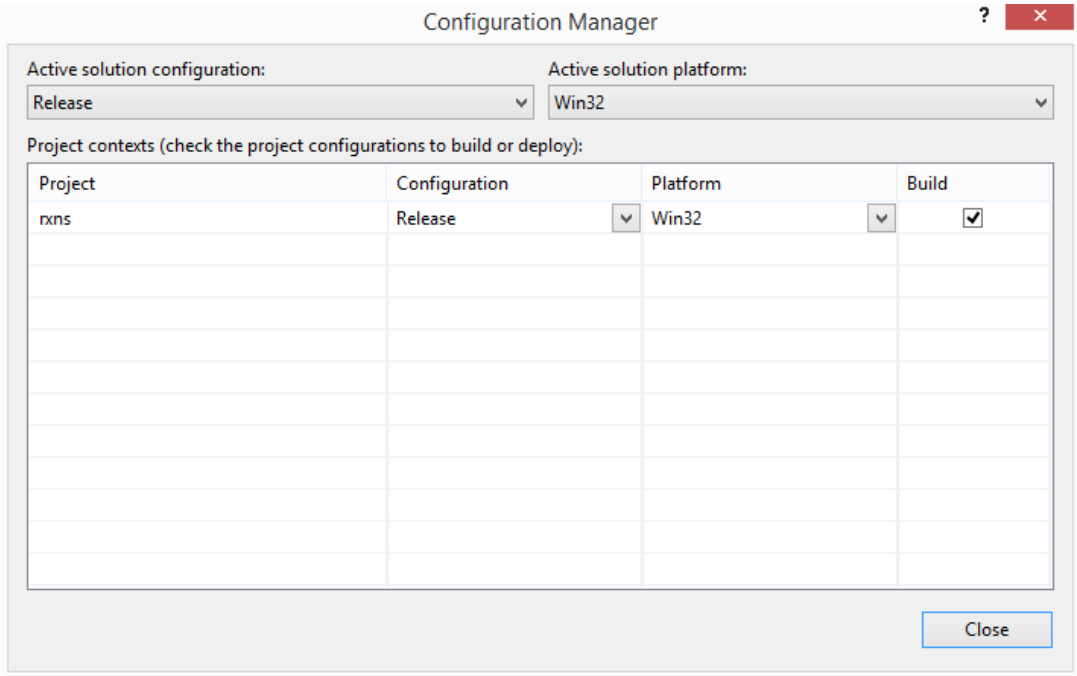


Figure A.3. Configuration manager of Microsoft Visual Studio 2010 Shell, used to set the proper configuration of the compiled dll.

b. Note if this is not done and the dll is compiled in a different configuration, such as X64, the following runtime error will occur when running the application using the GMS provided RT3D executable:
    i. The application was unable to start correctly (0xc000007b). Click OK to close the application.
    ii. This error can also result if Block 2 of the user defined subroutine starts with !DEC$ ATTRIBUTES DLLEXPORT :: rxns instead of !MS$ATTRIBUTES DLLEXPORT :: rxns. See correct version below, Table A.1.

5. Change the calling convention to CVF (/iface:cvf)
    a. Project (located in the top toolbar)> Properties > Fortran > External Procedures > Calling Convention > CVF(/iface:cvf), see Figure A.4 > Click Apply > Click Ok

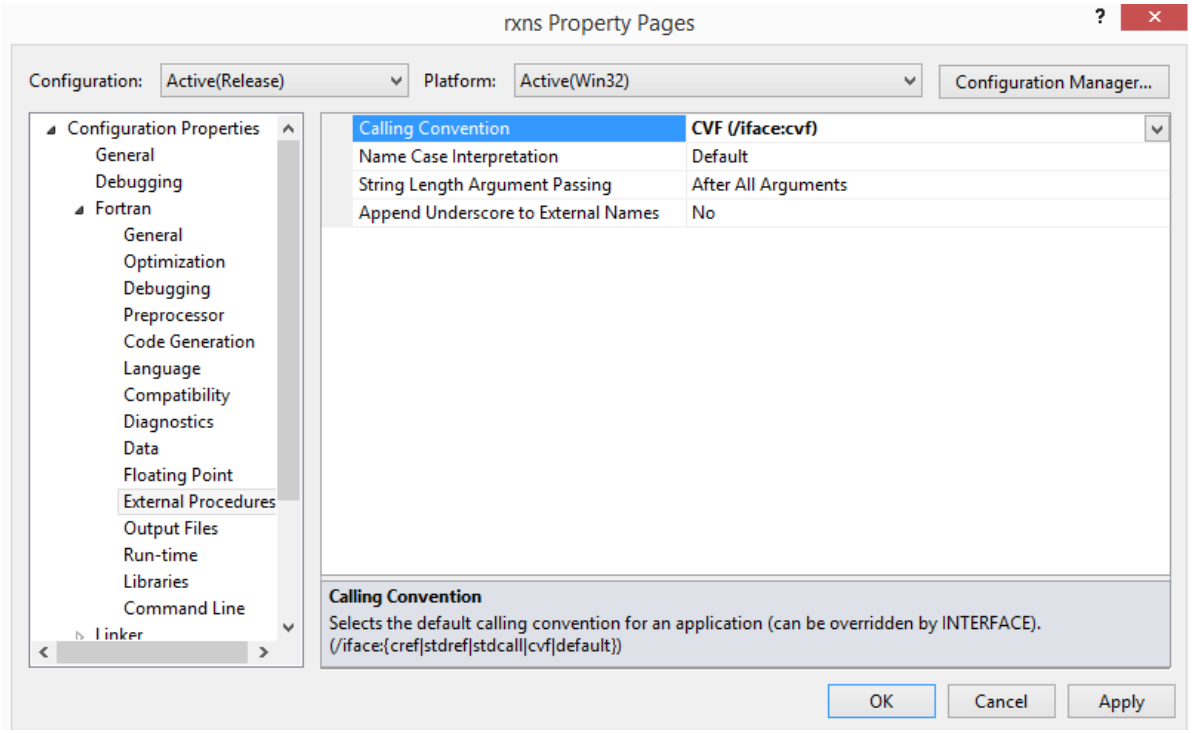


Figure A.4. Figure displaying properties of the project containing the Fortran user defined file.

    b. Note if this is not done and the dll is compiled then the following runtime error will occur when running the GMS provided RT3D executable:
        i. The procedure entry point_RXNS@60 could not be located in the dynamic link library.

6. Before compiling the user defined Fortran subroutine make sure to define all rate constants and other constants outside the if statement in Block 4 and place the rate constants in Block 5. If this is not done, RT3D will not initialize rate constants. A corrected version of Fortran file for a TCE > DCE > VC sequential is shown below. This is the same version as the one used in Chapter 2 Section 5. These edits can be made either outside or inside the Visual Studio. Finally, compile the dll using the build option in Visual Studio.
7. In order to build a solution, i.e. a dll, proceed as follows:

a. Build (located in the top tool bar) > Build solution > A build succeeded message will be displayed by Visual Studio > The dll related to the user defined subroutine will be in location used by user in Figure A.1 in a folder called Release > The dll will be named rxns.dll > To test the dll in batch mode or the full model the user can access instructions in Appendix C and Appendix B, respectively.
b. The user can build a new solution, using instructions in instruction number 7a, if desired, but first the user must clean the old solution by clicking Build (located in the top tool bar) > selecting clean solution.

Table A.1. Contains the user defined script referenced in instruction number 6.

```
      SUBROUTINE rxns(ncomp,nvrxndata,j,i,k,y,dydt,
     &     poros,rhob,reta,rc,nlay,nrow,ncol,vrc)
c ***** Block 1: Comments block *******
c234567890123456789012345678901234567890123456789012345678901234567890123456789012
c ncomp - Total number of components
c nvrxndata - Total number of variable reaction parameters to be input via RCT file
c J, I, K - node location (used if reaction parameters are spatially variable)
c y - Concentration value of all component at the node [array variable y(ncomp)]
c dydt - Computed RHS of your differential equation [array variable dydt(ncomp)]
c poros - porosity of the node
c reta -  Retardation factor [array variable reta(mcomp)]
c rhob -  bulk density of the node
c rc - Stores spatially constant reaction parameters (up to 100 values)
c nlay, nrow, ncol - Grid size (used only for dimensioning purposes)
c vrc - Array variable that stores spatially variable reaction parameters
c ***** End of Block 1 *******

c *** Block 2: Please do not modify this standard interface block ***
      !MS$ATTRIBUTES DLLEXPORT :: rxns
      IMPLICIT NONE
      INTEGER ncol,nrow,nlay
      INTEGER ncomp,nvrxndata,j,i,k
      INTEGER First_time
      DATA First_time/1/
      DOUBLE PRECISION y,dydt,poros,rhob,reta
      DOUBLE PRECISION rc,vrc
      DIMENSION y(ncomp),dydt(ncomp),rc(50)
      DIMENSION vrc(ncol,nrow,nlay,nvrxndata),reta(50)
C ****** End of block 2 *******

C *** Block 3: Declare your problem-specific new variables here ***
C     INTEGER
      DOUBLE PRECISION tce,dce,vc,kpce,ktce,kdce,kvc
C ***** End of Block 3  ******
```

Table A.1 (cont.). Contains the user defined script referenced in instruction number 6.

```
C *** Block 4: Initilize reaction parameters here, if required ***
      IF (First_time .EQ. 1) THEN
        First_time = 0 !reset First_time to skip this block later
      END IF
C ***** End of Block 4  ******

C  *** Block 5: Definition of other variable names ***
       tce = y(1)
       dce = y(2)
       vc = y(3)
       ktce = rc(1)
       kdce = rc(2)
       kvc = rc(3)
C ***** End of Block 5  ******

c  *** Block 6: Definition of Differential Equations ***
       dydt(1) = -ktce*tce/reta(1)
       dydt(2) = (-kdce*dce + ktce*tce)/reta(2)
       dydt(3) = (-kvc*vc + kdce*dce)/reta(3)
C ***** End of Block 6  ******
      RETURN
      END
```

Appendix B. Step by Step Modeling Instructions using GMS

This appendix provides instructions for creating the 2-D flow cell described in Chapters 2 and 3 using GMS version 10.2. Appendix B.1 contains the instructions for creating the MODFLOW model. Appendix B.2 and B.3 contain the instructions for RT3D model described in Chapter 2 and Chapter 3, respectively.

B.1 GMS MODFLOW Tutorial

1. Open GMS
2. In the Project Explorer (to locate the project explorer check the GMS website http://www.xmswiki.com/wiki/GMS:Project_Explorer) right click and select New > 3d grid > The window shown in Figure B.1. will appear> Enter the values as shown in Figure B.1. > Click OK

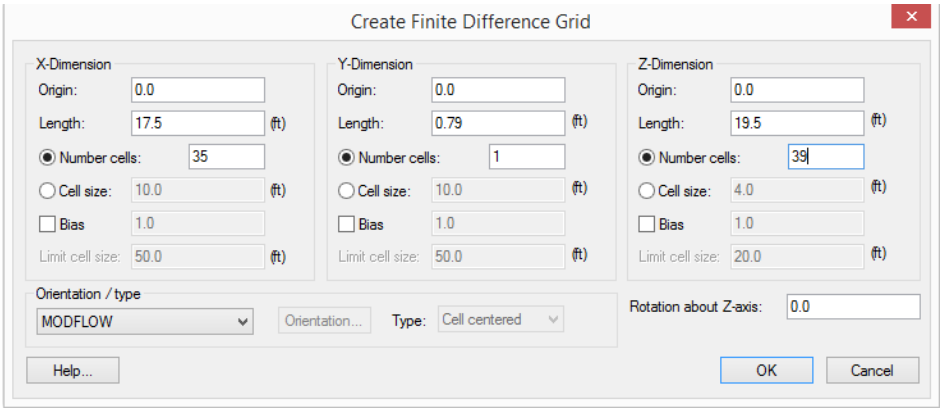


Figure B.1. Figure shows the window used to create the finite difference model, used in instruction number 2 in Chapter B.1. The user can define model dimensions in this window.

3. Right Click Grid in the Project Explorer> New MODFLOW > Select all the values as shown in Figure B.2:

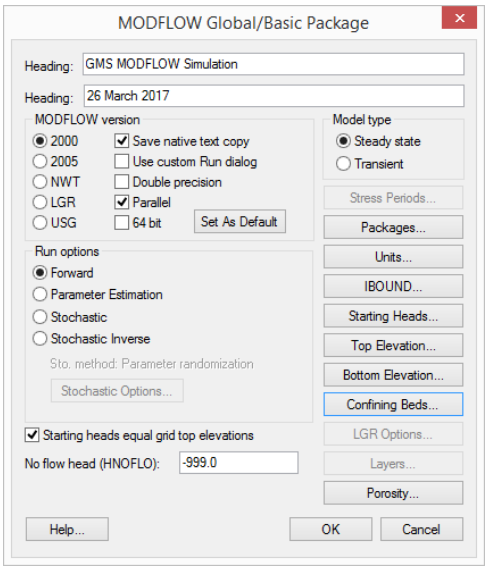


Figure B.2. MOFLOW Global/Basic package window.

4. Check Save native text copy in the MODFLOW Global/Basic package window. This will save a version of MODFLOW input files that are accessible outside of GMS. Most are already checked by default and details for other settings can be displayed using the help option located at the bottom left of the MODFLOW Global Basic Package.
5. Click units, change Mass to g and Concentration to moles/liter in the MODFLOW Global/Basic package window. MODFLOW and RT3D doesn't require units to be set as long as the units are consistent. These units only serve as a reminder for the modeler to input the correct values. Units window shown in Figures B.3.

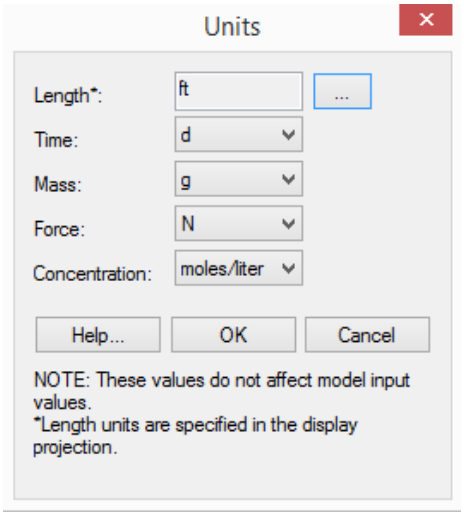


Figure B.3. Units window located in the MODFLOW Global/Basic package window.

6. Click … next to Length and change length to inches (see Figure B.4).

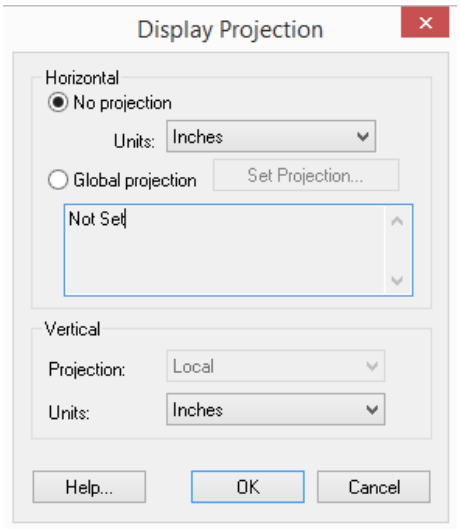


Figure B.4. Used to set units for distance. Note distance units need to be defined at two locations in this window.

7. Click ok until you have reached the model screen. The model screen will display the initial model grid. Model screen will be similar to the image shown in Figure B.6.
8. Change the view and select all cells. Change the VK/VANI ratio to 1 by right clicking on the selected cells > Properties > MODFLOW tab> VK/VANI > 1.0 . This will make the vertical and horizontal hydraulic conductivity the same. Select cells by clicking  and change the view using  . Properties window shown in Figure B.5.

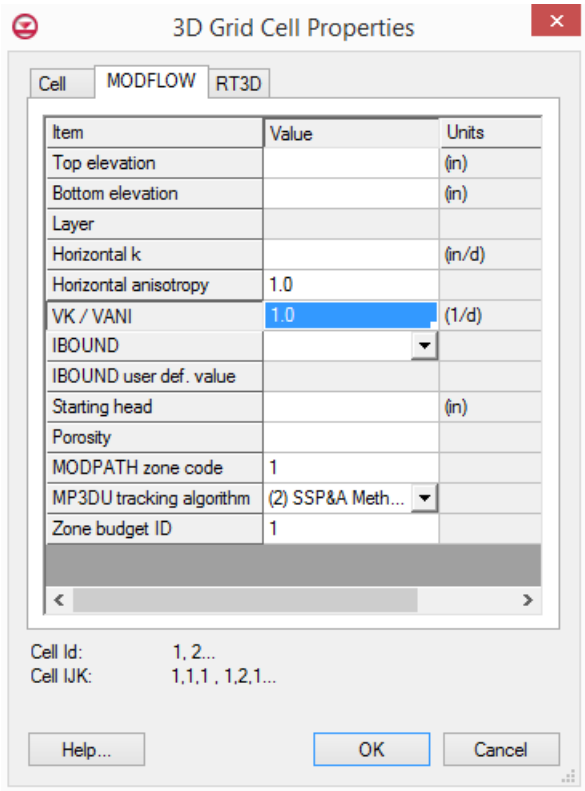


Figure B.5. Window used to define the VK/VANI ratio.

9. Change the view and select all cells included in layers 1 through 27. This will be the high permeability zone (HPZ), shown in the selected cells (blue) in Figure B.6.

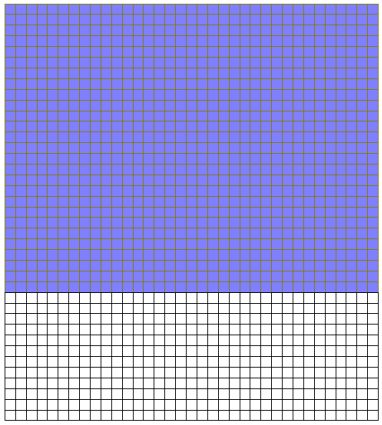


Figure B.6. Image shows the finite difference grid setup using steps 1 through 9 in Chapter B.1. The blue cells are highlighting the HPZ.

10. Change the hydraulic conductivity and porosity to the values listed below. Right click selected cells > Properties > MODFLOW tab > Horizontal k > 34.015 in/d (see Figure B.7). Leave the rest the same.

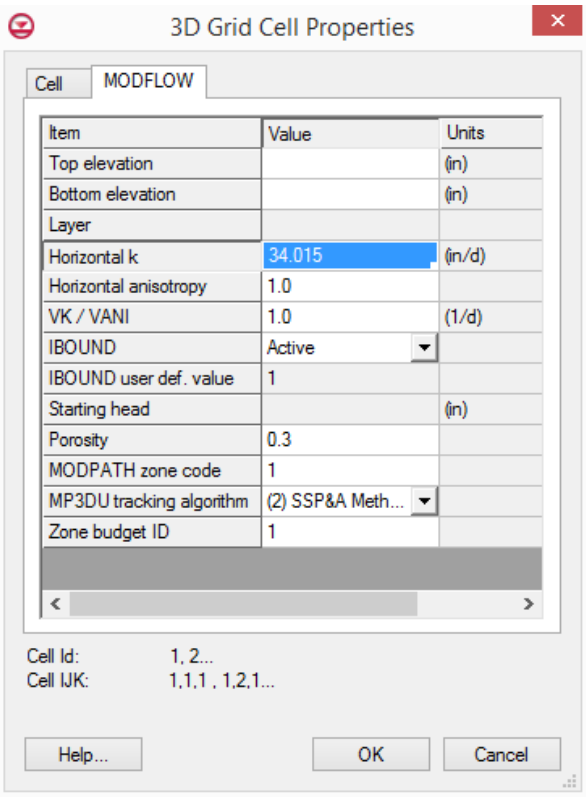


Figure B.7. Highlighted is the input cell used to set the horizontal hydraulic conductivity.

11. Change the porosity in the same window as step 11(see above) to 0.31 > Click OK.
12. Select 1,1,28 to 1,1,39 while keeping I and J positions constant. Make IBOUND 0, this will make these cells inactive. Right click selected cells > Properties > MODFLOW Tab > IBOUND > Inactive> Click OK.

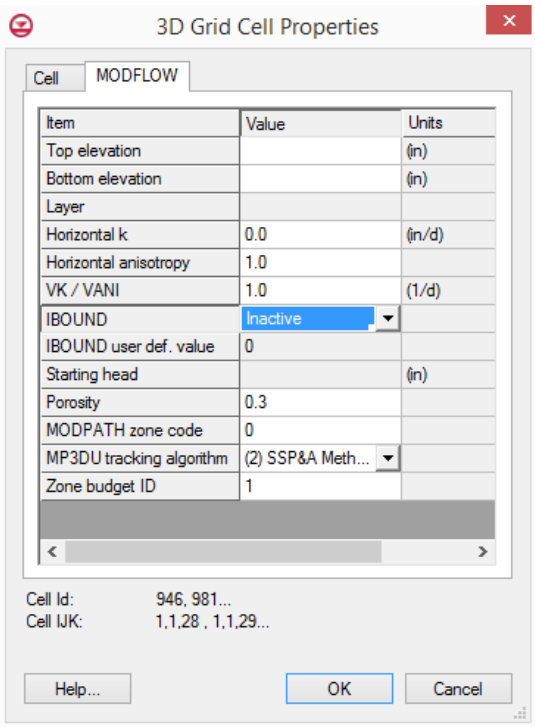


Figure B.8. Highlighted cell used to create inactive cells in MODFLOW.

13. Similarly select 1,35,28 to 1,35,39: keeping I and J positions constant. Make IBOUND 0, this will make these cells inactive > Click OK. The model will now look like the one shown in Figure B.9.
14. The remaining region is the low permeability zone, LPZ (shown in blue in Figure B.9). Change the horizontal hydraulic conductivity to 0.00340157 in/day and porosity to 0.06. Select the LPZ cells > Right click selected cells > MODFLOW tab > change horizontal hydraulic conductivity and porosity > Click OK. Window used to change the horizontal hydraulic conductivity and porosity in shown in Figure B.10.

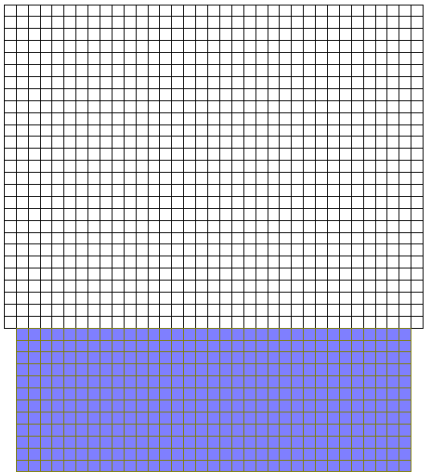


Figure B.9. Figure shows model view of the finite difference grid after following steps 1 through 14 in Chapter B.1. Blue cells are the selected cells of the LPZ.

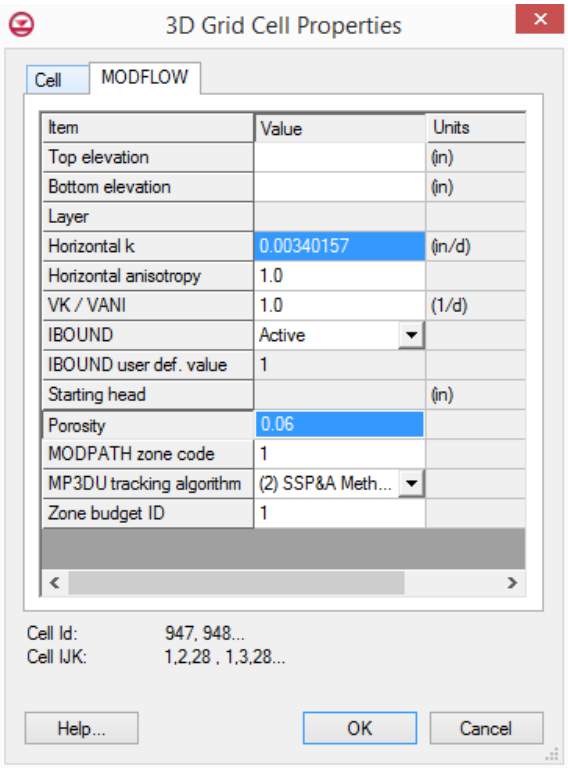


Figure B.10. Window shows the values changed of porosity and hydraulic conductivity for the LPZ. Highlighted cells are locations where the values are changed.

15. The flow domain will now look like Figure B.11.

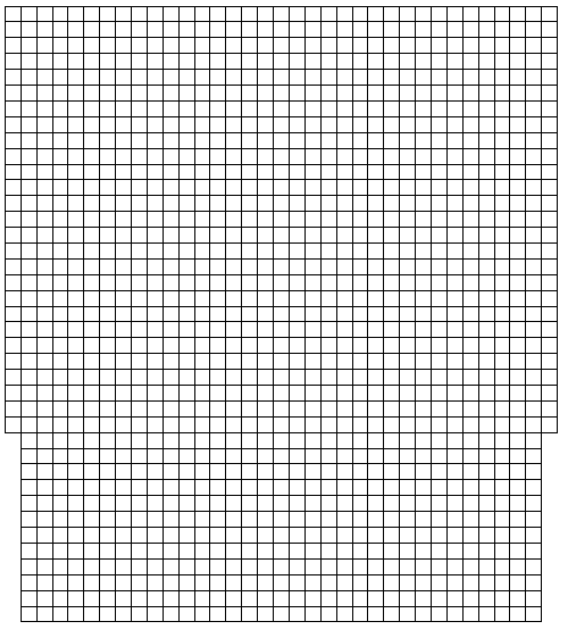


Figure B.11. Finite difference grid shown after following steps 1 through 14 in Chapter B.1.

16. At the cells 1,2,28 through 1,34,28 or the HPZ/LPZ interface add three more layers using  . This will refine the grid and provide greater accuracy near the HPZ-LPZ interface. The sum total of layers will now become 42 and the grid will look like so (Figure B.12):

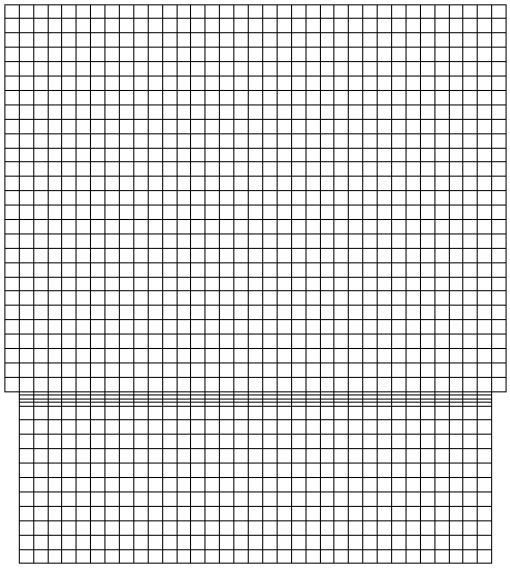


Figure B.12. Refined finite difference grid created by following instruction 16 for Chapter B.1.

17. Select cells 1,1,1 to 1,1,27, keeping I and J constant. Change IBOUND to specified head and change starting head to 25 in by right clicking on the selected cells and clicking properties followed by MODFLOW tab, then select as follows:

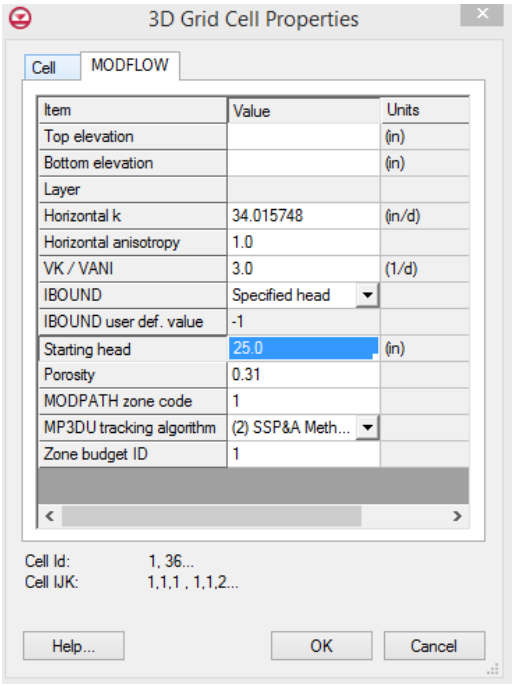


Figure B.13. Properties window used to set a constant head boundary at the entrance of the HPZ.

18. Click OK
19. Similarly select 1,35,1 to 1,35,27, by keeping the I and J constant. Change the head to 24.5 in. The model will now look as follows (Figure B.14):

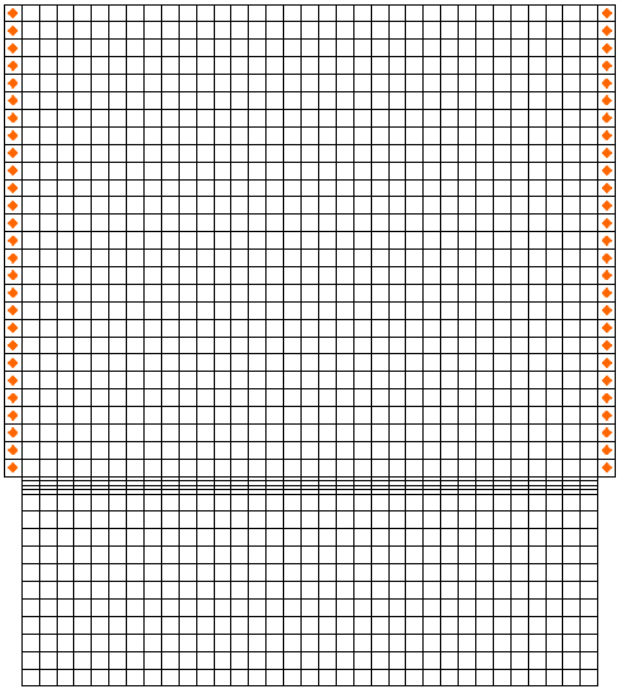


Figure B.14. Finite difference model after following steps 1 through 19 of Chapter B.1.

20. Lastly run the model by clicking  , save the model if necessary.
21. Results are shown below, Figure B.15.

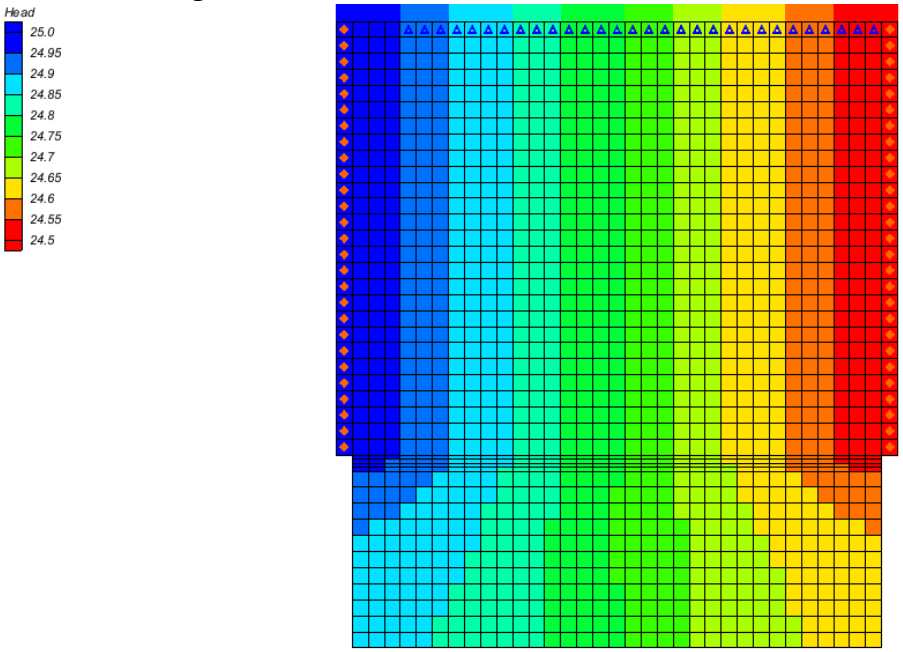


Figure B.15. MODFLOW simulation results.

B.2 RT3D model setup

Prior to using these instructions, the user must have compiled a dll for the user defined reaction in Chapter 2. Instructions for compiling a dll are provided in Appendix A. These instructions assume the user has created the MODFLOW simulation described in B.1.

1. In the Project Explorer, right click Grid > New MT3DMS
2. Basic Transport Package > Model > RT3D
3. To select the RT3D packaged follow: Basic Transport Package > Packages > Select as follows (Figure B.16)> Note the GCG solver values are kept default, details in MT3DMS manual (Zheng et al., 1999)

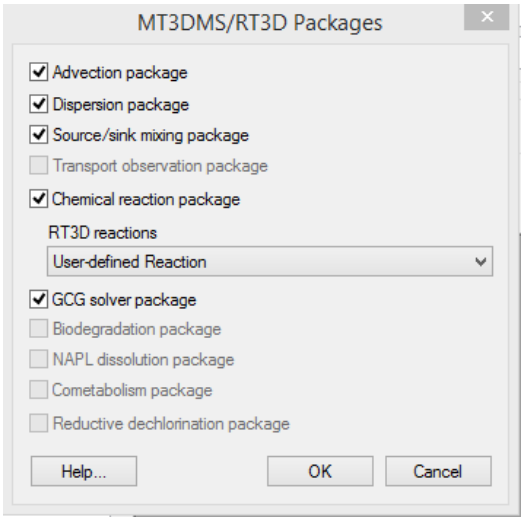


Figure B.16. Window shows selected RT3D packages.

4. Click ok
5. Basic Transport Package > Define Species > Click New 5 times for the 5 species used in this user defined subroutine> Name species in the same order as shown below, Figure B.17 (Note: define species must be organized in such a way that the species are in the same order as Block 5 of the user defined subroutine).

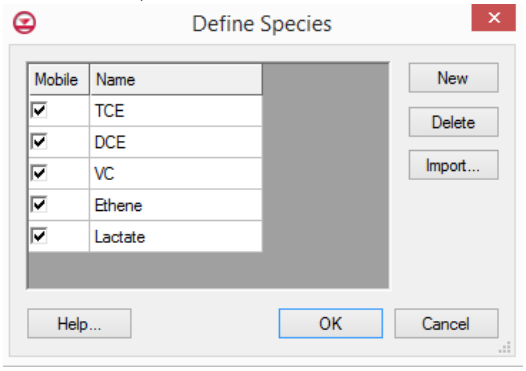


Figure B.17. Figure shows the order of the defined species.

6. Click OK
7. Basic Transport Package > Stress Periods (setup window shown in Figure B.18)

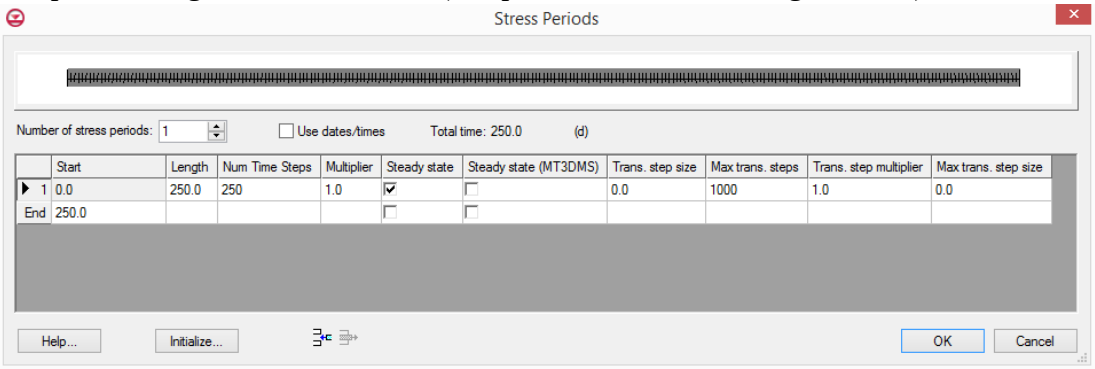


Figure B.18. Figure indicates the length of the simulation at 250 days.

8. Click OK
9. The final Basic Transport Package Window will look as so (Figure B.19):

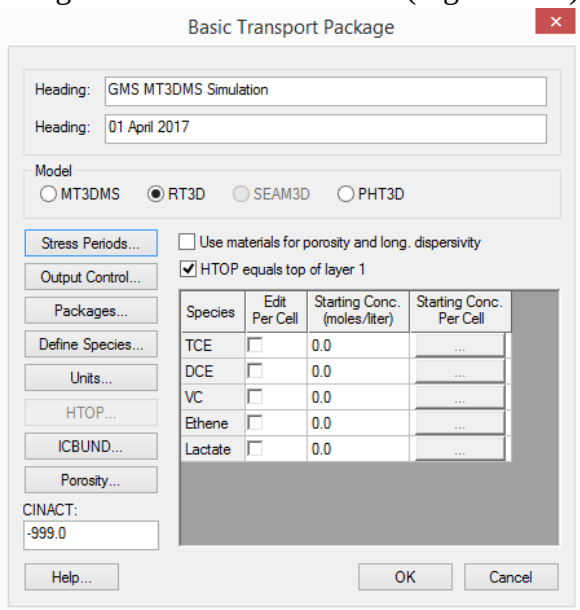


Figure B.19. Figure shows Basic Transport Package window.

10. Click OK
11. Right Click MT3DMS Dispersion Package MT3DMS > DMCOEF > 0.04874698 in^2/day. The DMCOEF, diffusion coefficient, must be entered separately for each layer in window shown in Figure B.20.

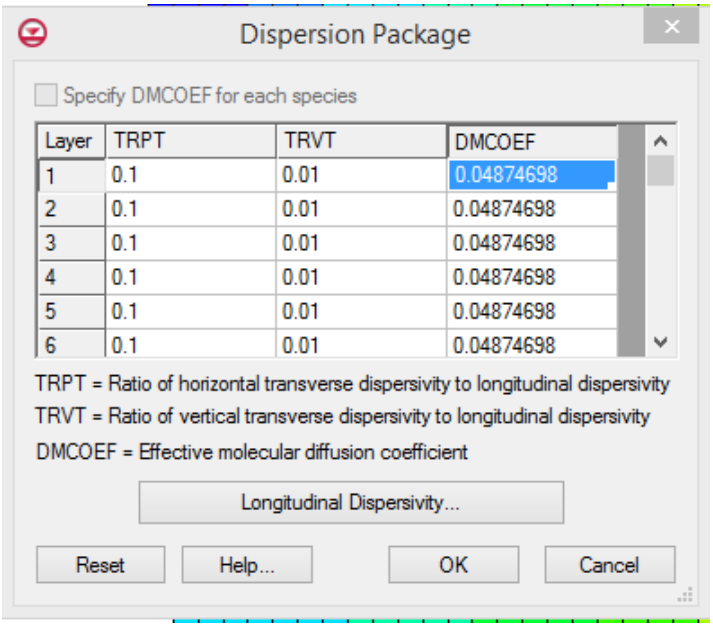


Figure B.20. Figure shows location for each layer where the diffusion coefficient is defined.

12. Keep the remaining values unchanged in the dispersion package. Click OK.
13. Select all the cells in the HPZ. Right click the selected cells > Properties > RT3D tab > Change porosity to 0.31.

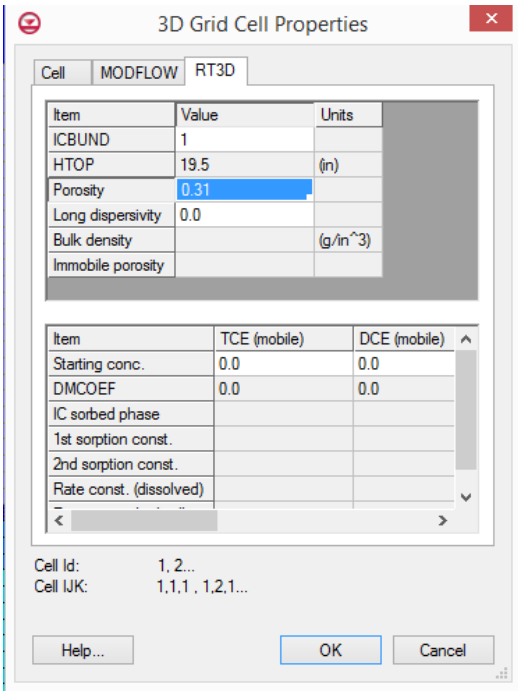


Figure B.21. Window shows the input cell used to change the porosity in the HPZ.

14. Select all the cells in the LPZ. Similarly, change porosity to 0.06.
15. Select 1,2,42 to 1,34,42 while keeping I and K constant. Right click the selected cells > Source and Sink > RT3D : Point SS > Add BC > Change All TCE concentration to 0.009

mol/l > Change ITYPE All to constant concentration> Make sure the ITYPE is constant concentration and concentration values for TCE are 0.009 mol/l while for other species the values are zero for all the selected cells> Click OK. Source/Sink input window will look the one shown in Figure B.22.

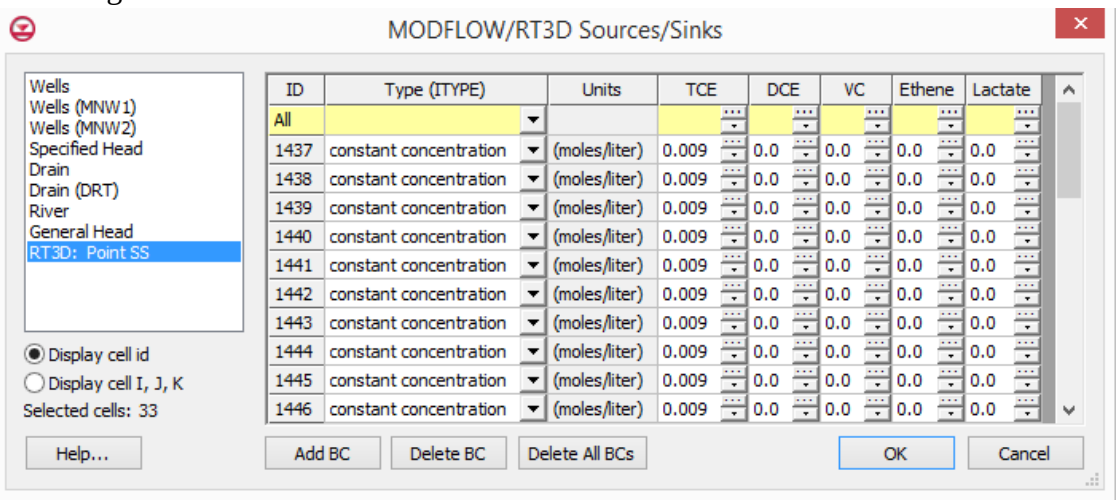


Figure B.22. Figure shows the setup used to set a constant concentration boundary at the bottom of the LPZ.

16. Right click the above selected cells > Properties > RT3D tab > Change ICBUND to -1 (see Figure B.23). Note a negative value means constant concentration. This is overridden by the ITYPE but just as a precaution change the value to -1.

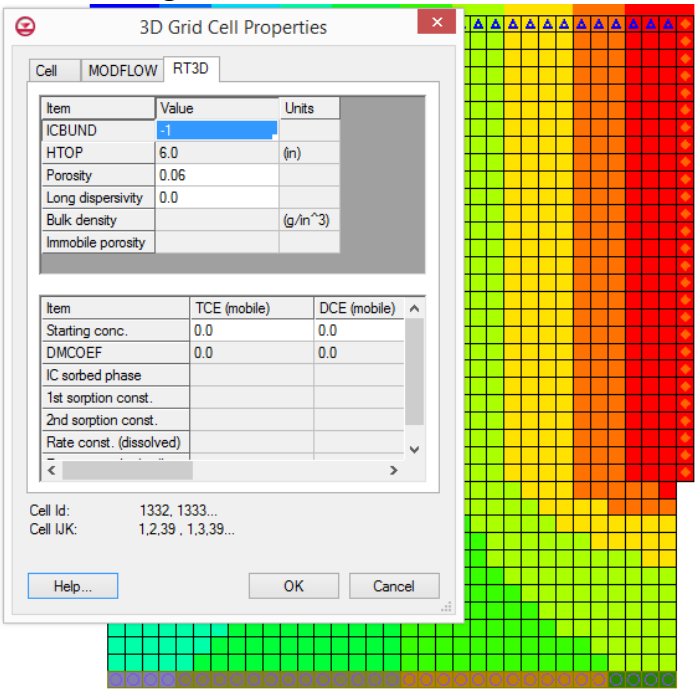


Figure B.23. Figure sets the cells, located at the bottom of the LPZ, as constant concentration.

17. Select 1,1,1 to 1,1,27 while keeping I and J constant. Right click the selected cells > Source/Sinks > RT3D : Point SS > Add BC > Change All Lactate concentration to 0.001 mol/l > Change ITYPE All to constant concentration> Make sure the ITYPE is constant concentration and concentration values for lactate are 0.001 mol/l while for other species the values are zero for all the selected cells > Click OK.
18. Right click the above selected cells > Properties > RT3D tab > Change ICBUND to -1 > Click OK. Note a negative value means constant concentration. This is overridden by the ITYPE but just as a precaution change the value to -1.
19. Right Click MT3MS icon MT3DMS > Select Chemical Reaction Package > Define parameters > Click New three times to add three different rate constants > Select spatially variable > Click OK. Note parameters need to be in the same order as the user defined package. The final Chemical Reaction Package window is shown in Figure B.24. The window used to define the rate constants is shown in Figure B.25.

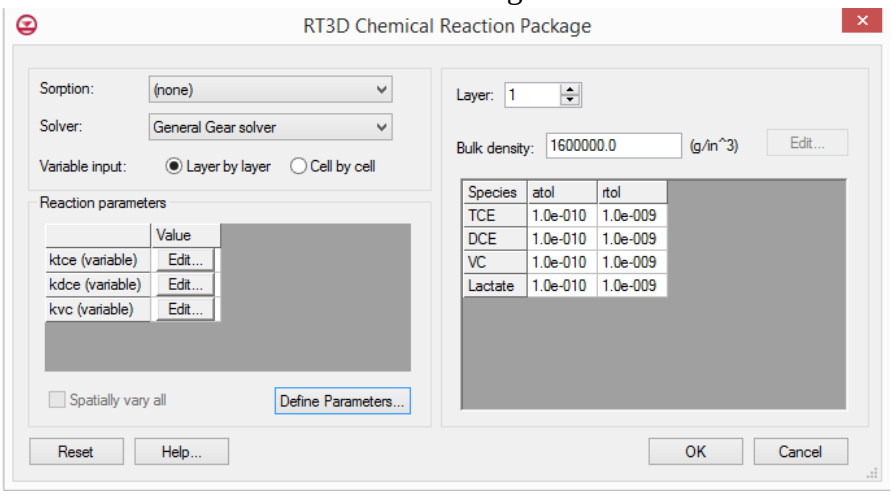


Figure B.24. Figure shows the final Chemical Reaction Package Window.

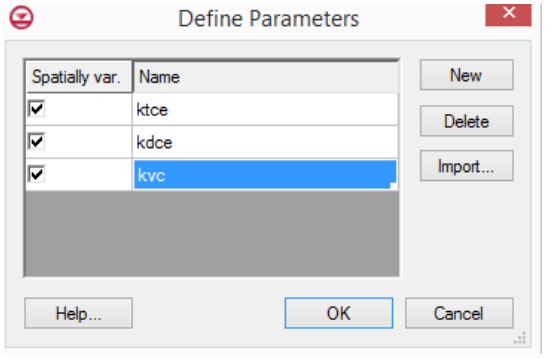


Figure B.25. Figure defines the rate constants used in Chapter B.2.

20. Select all the cells in the LPZ > Properties > RT3D tab > ktce = 432 L/(mol*day) > kdce = 259.2 L/(mol*day) > kvc = 86.4 L/(mol*day) > Click OK. Input panel shown in Figure B.26.

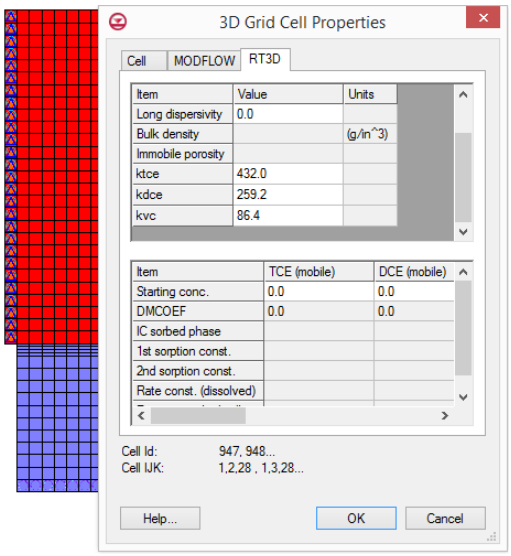
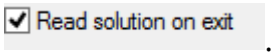


Figure B.26. Figure shows the locations in the input panel used to set the rate constants.

21. Move the user defined dll (see instructions in Appendix A) into the directory containing GMS rt3d version. This will most likely be located at C:\Program Files\GMS 10.2 64-bit\models\rt3d, i.e. the GMS install directory. Before moving the user defined rxns.dll file rename the provided rxns.dll and jacrxns.dll to rxns_old.dll and jacrxns_old.dll. The jacrxns file is created by the user and is used by RT3D in case of stiff systems, details in RT3D manual (Clement, 2002). Jacrxns file is not created for our simple system.
22. Run RT3D by clicking  and save the file if necessary.
23. After running RT3D select 

.
24. To see the results, click the chemical species shown in Figure B.27.

Figure B.27. Figure shows the available species for which the concentrations results can be viewed in GMS. Click on the species to view the results.

B.3 RT3D model setup

Prior to using these instructions, the user must have compiled a dll for the user defined reaction in Chapter 3. Instructions for compiling a dll are provided in Appendix A. These instructions assume the user has created the MODFLOW simulation described in B.1.

1. In the Project Explorer, right click Grid 

> New MT3DMS
2. Basic Transport Package > Model > RT3D

3. Basic Transport Package > Packages > Select as follows (Figure B.28) > Note the GCG solver values are kept default, details in MT3DMS manual (Zheng et al., 1999)

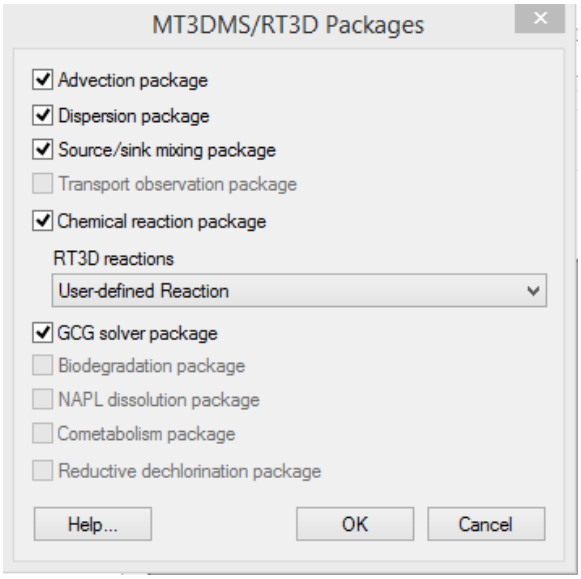


Figure B.28. Window shows selected RT3D packages.

4. Click ok
5. Basic Transport Package > Define Species > Click New 8 times to define the 8 species used by this model> Name species in the same order as shown below in Figure B.29 (Note: define species must be organized in such a way that the species are in the same order as the user defined subroutine Block 5).

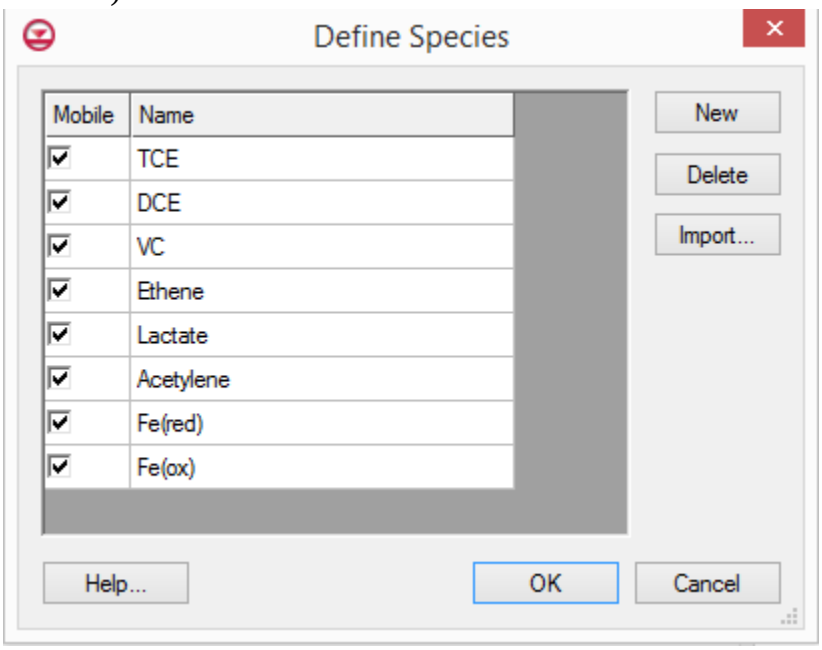


Figure B.29. Figure shows the order of the defined species for Chapter 3 in GMS.

6. Click OK

7. Basic Transport Package > Stress Periods > Change the figure as follows (see Figure B.30)

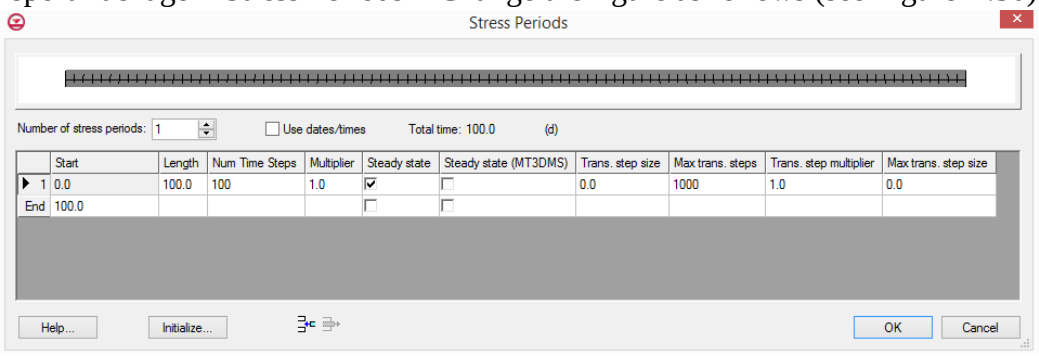


Figure B.30. Figure show the length of the stress period set at 100 days.

8. Click OK
9. The final Basic Transport Package Window will look as so (Figure B.31):

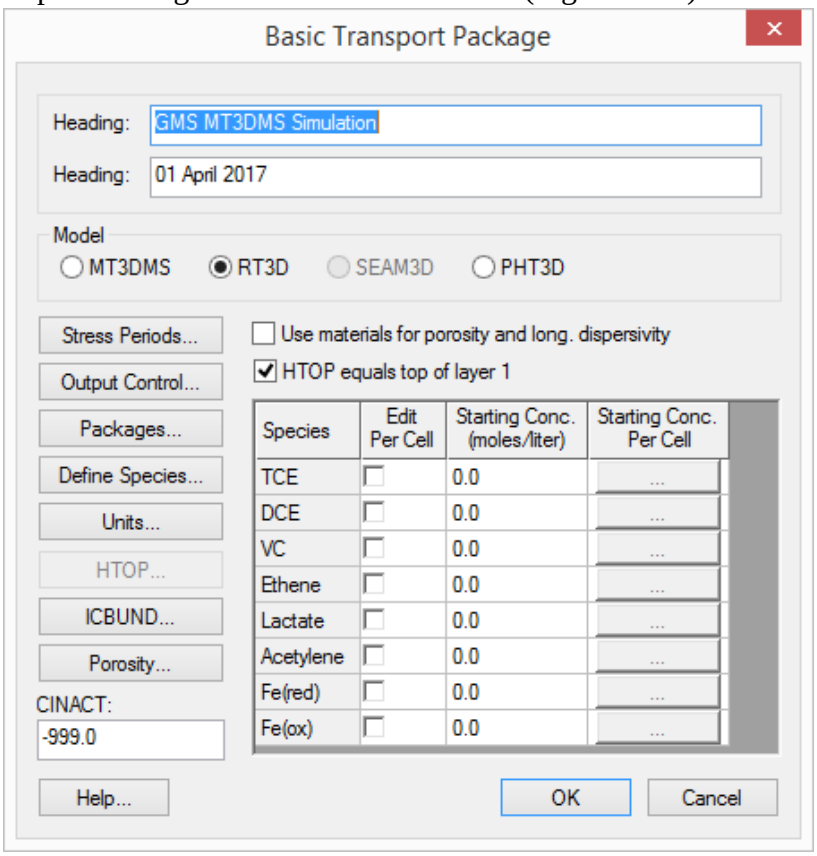


Figure B.31. Figure shows the Basic Transport Package window.

10. Click OK
11. Right Click MT3DMS Dispersion Package MT3DMS > DMCOEF > Change the value to 0.04874698 in^2/day for all layers. Figure B.32 shows the dispersion package.

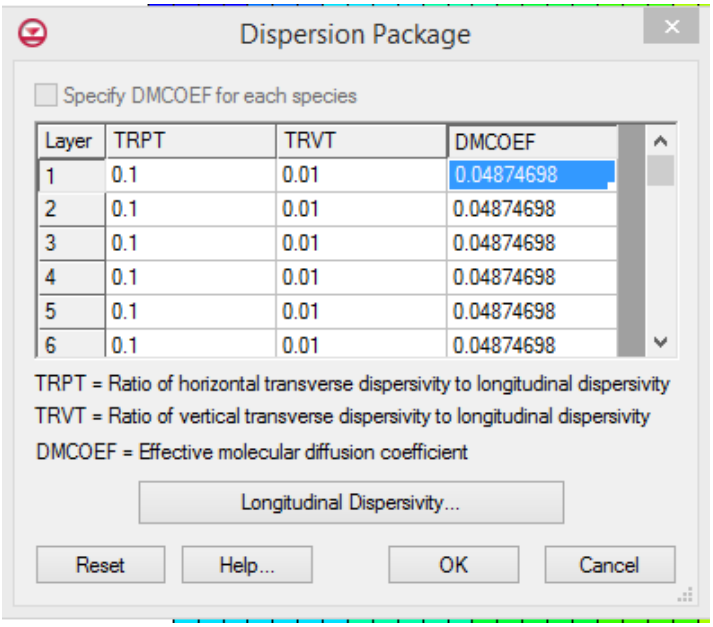


Figure B.32. Figure highlights the input cell used for layer 1 where the diffusion coefficient is defined.

12. Keep the remaining values unchanged in the dispersion package. Click OK.
13. Select all the cells in the HPZ. Right click the selected cells > Properties > RT3D tab > Change porosity to 0.31 (Figure B.33).

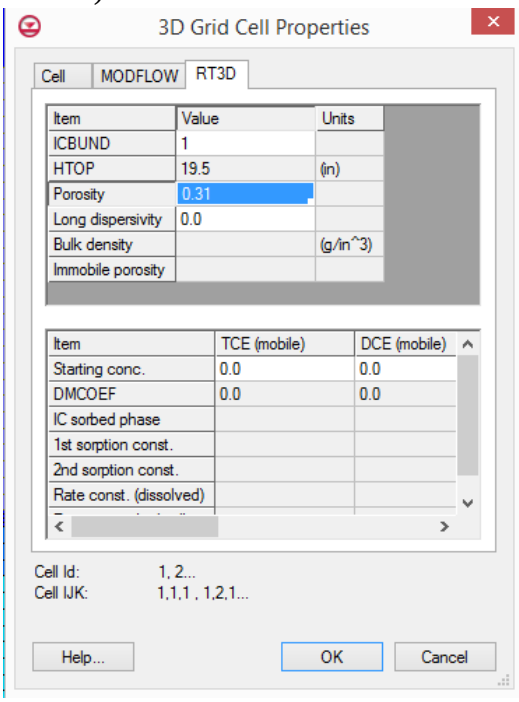


Figure B.33. Window shows the input cell where HPZ porosity is set.

14. Select all the cells in the LPZ. Similarly, change porosity to 0.06.

15. Select 1,2,42 to 1,34,42 while keeping I and K constant. Right click the selected cells > Source and Sink > RT3D : Point SS > Add BC > Change All TCE concentration to 0.009 mol/l, keep other at 0.0 mol/l > Change ITYPE All to constant concentration> Make sure the ITYPE is constant concentration and concentration values for TCE are 0.009 mol/l while for other species the values are zero for all the selected cells> Click OK. Source/Sink input window will look the one shown in Figure B.34.

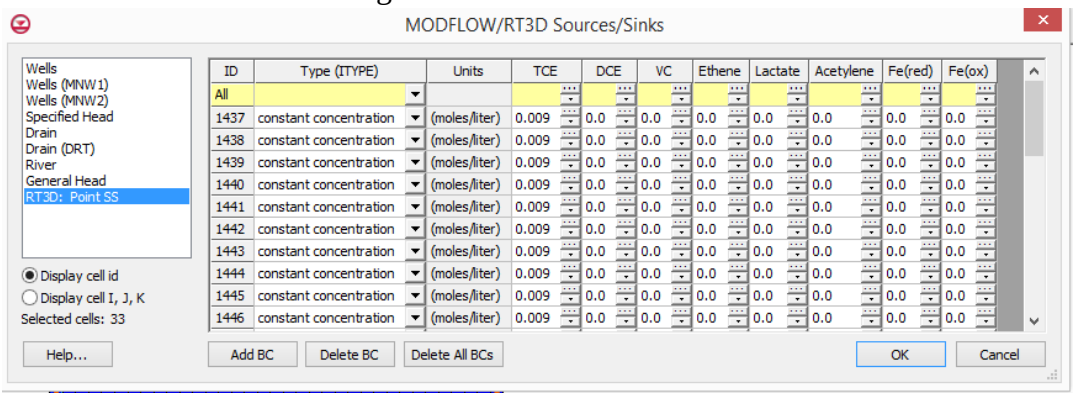


Figure B.34. Figure shows the source/sinks package window used to set the constant concentration boundary condition at the bottom of the LPZ.

16. Right click the above selected cells > Properties > RT3D tab > Change ICBUND to -1 (Figure B.35) > Click Ok. Note a negative value means constant concentration. This is overridden by the ITYPE but just as a precaution change the value to -1.

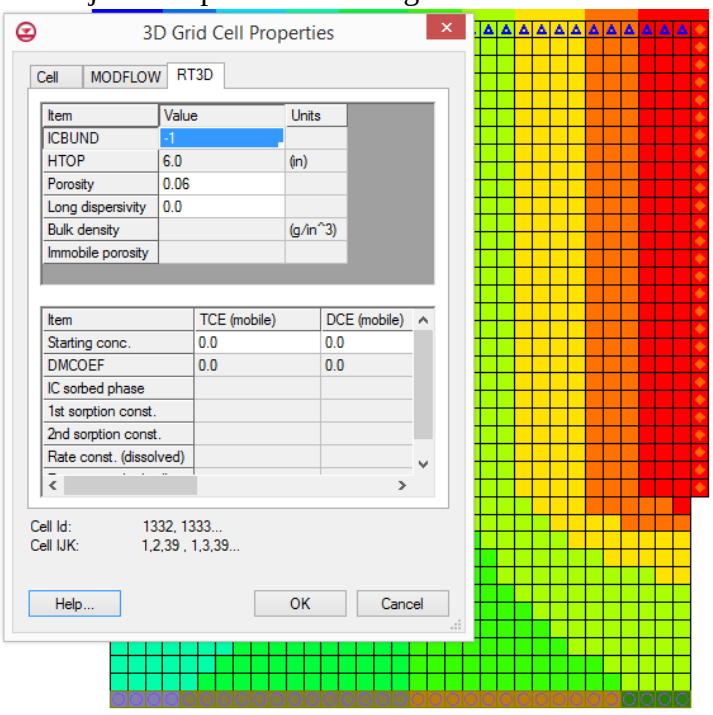


Figure B.35. Properties window used to set the selected cells at the bottom of the LPZ as constant concentration.

17. Select 1,1,1 to 1,1,27 while keeping I and J constant. Right click the selected cells > Source/Sinks > RT3D : Point SS > Add BC > Change All Lactate concentration to 0.001 mol/l > Change ITYPE All to constant concentration> Make sure the ITYPE is constant concentration and concentration values for lactate are 0.001 mol/l while for other species the values are zero for all the selected cells > Click OK. Source/Sink input window will look the one shown in Figure B.36.

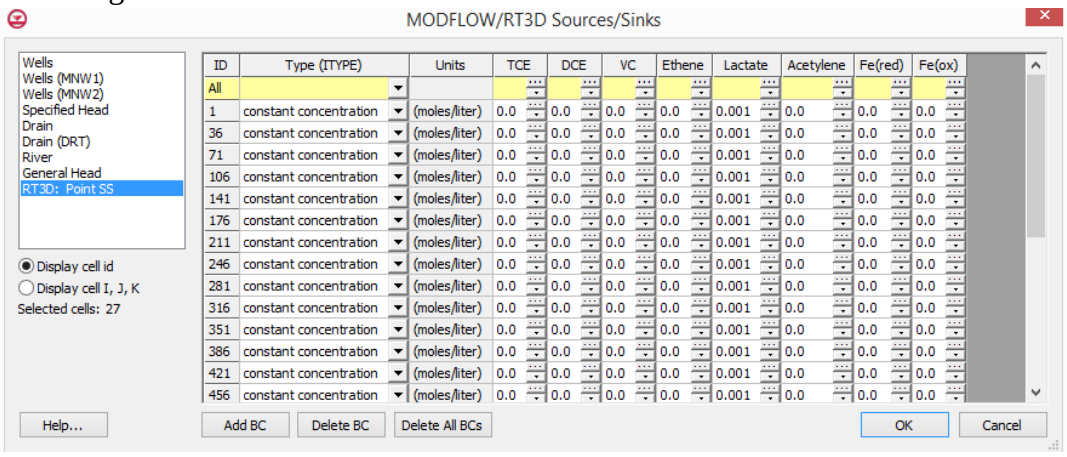


Figure B.36. Figure shows the source/sinks package window used to set the constant concentration boundary condition at the entrance nodes of the HPZ.

18. Right click the above selected cells > Properties > RT3D tab > Change ICBUND to -1 > Click OK. Note a negative value means constant concentration. This is overridden by the ITYPE but just as a precaution change the value to -1.
19. Right Click MT3MS icon MT3DMS > Select Chemical Reaction Package > Define parameters > Click New five times to add five different rate constants > Select spatially variable > Click OK. Note parameters need to be in the same order as the user defined package (the order is in Block 5 of the user defined subroutine). Figure B.37 shows the Chemical Reaction package window after defining rate constants. Rate constants are defined in Figure B.38.

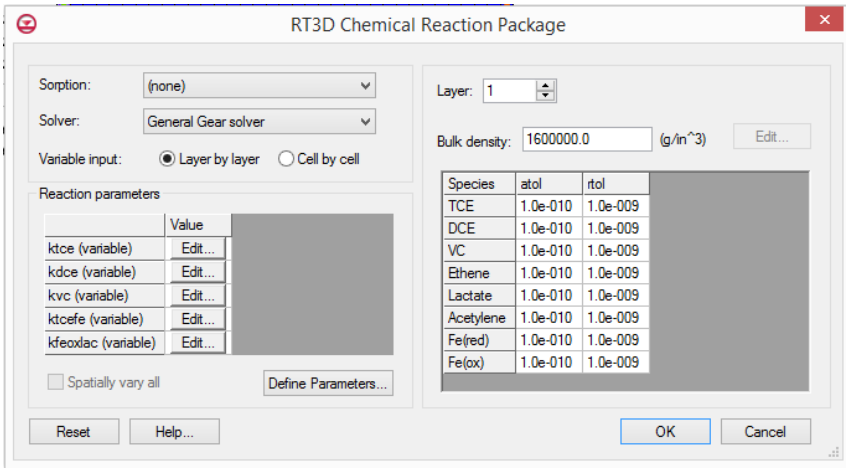


Figure B.37. Window shows the Chemical Reaction package.

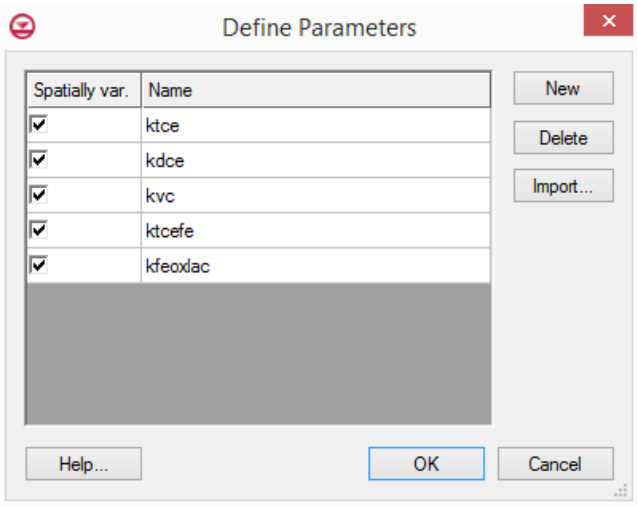


Figure B.38. Figure shows the order of the rate constants defined in the Chemical Reactions package window.

20. In the same Chemical Reaction Package window, Figure B.37, change sorption to linear isotherm (Figure B.39)> For layers 27 through 42 enter 1E9 for the 1st sorption constant column for Fe(red). This will simulate Fe(red) as an immobile species. Layers are changed by entering the layer number next to the input dialog stating Layer (highlighted in Figure B.39). Example setup for layer 27 is shown below> Click Ok to exit the Chemical Reaction Package once all the 1st sorption constants for Fe(red) in layers 27 through 42 are set a 1E9.

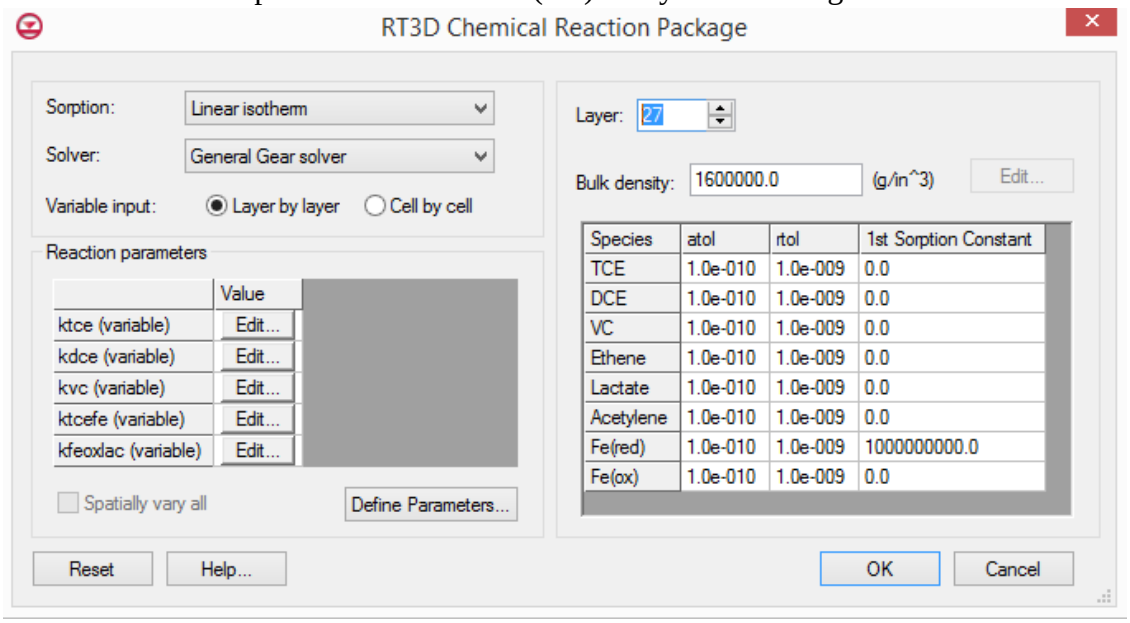


Figure B.39. Final Chemical Reactions package window. Also indicates the sorption constants for layer 27. Highlighted cell is the location where layer numbers can be entered.

21. Select all the cells in the LPZ > Properties > RT3D tab > ktce = 432 L/(mol*day) > kdce = 259.2 L/(mol*day) > kvc = 86.4 L/(mol*day) > ktcefe = 10 L/(mol*day) > kfeoxlac = 10 L/(mol*day) > Click OK. Properties window used to do this is shown in Figure B.40.

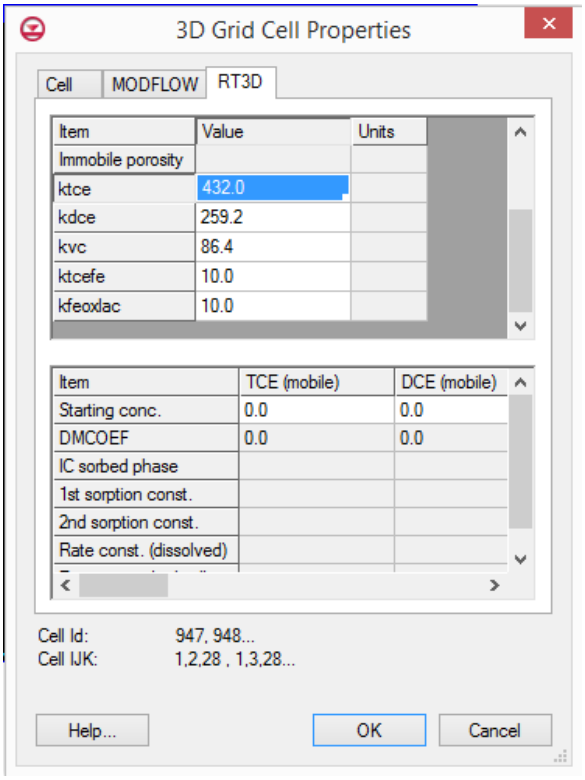


Figure B.40. Window shows the input locations used to set the rate constants.

22. Select all the cells in layers 28 through 41 in the LPZ to set the initial concentration of Fe(red)> Right Click > Properties > Starting conc. > Change the value of Fe(red) to 0.001 mol/l, leaving others 0 mol/l > Click OK. Figure B.41 highlights the location where the initial condition for Fe(red) is entered.

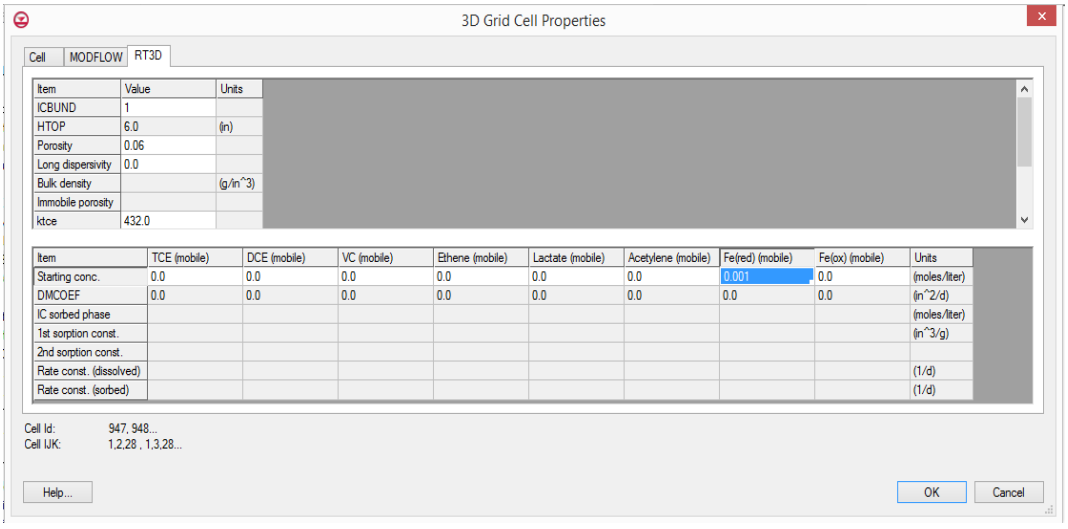
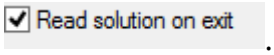


Figure B.41. Properties window shows the input location used to input the initial condition for Fe(red). Note this window is not used to set the DMCOEF for the simulation. The values of zero for the DMCOEF stated here are not used in the simulation.

23. Move the user defined dll (see compiling instructions in Appendix A) into the directory containing GMS rt3d executable, called rt3d25.exe. This will most likely be located at C:\Program Files\GMS 10.2 64-bit\models\rt3d, i.e. the GMS install directory. Before moving the user defined rxns.dll file rename the provided rxns.dll and jacrxns.dll to rxns_old.dll and jacrxns_old.dll. The jacrxns file is created by the user and is used by RT3D in case of stiff systems, details in RT3D manual (Clement, 2002). No jacrxns file was create for the case defined in Chapter 3.
24. Run RT3D by clicking  and save the file if necessary.
25. After running RT3D select 

.
26. To see the results, click the chemical species shown in Figure B.42.

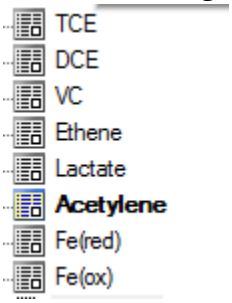


Figure B.42. Figure shows the available species for which the concentrations results can be viewed in GMS. Click on the species to view the results.

Appendix C. Instructions for Running RT3D Batch Mode

This appendix will explain how to run RT3D in batch mode in order to verify the compiled dll containing the user defined reaction. This appendix will specifically use the rt3dbat1.exe file provided with the GMS installation to run RT3D batch mode. The batch mode is run outside and independently of the entire GMS model run. Below are the instructions for running scenario 1, explained in Chapter 2, in batch mode where only TCE is present initially. Follow the steps below to test the user defined reaction dll defined in Chapter 2. In this test case, the batch utility was run using a Windows 8.1 64-bit computer.

1. Place the rt3dbat1.exe or the provided RT3D batch utility executable in the local directory containing user defined rxns.dll file. If the rxns.dll file is not available in the same directory as the batch utility and the batch utility is run then the following error will occur.

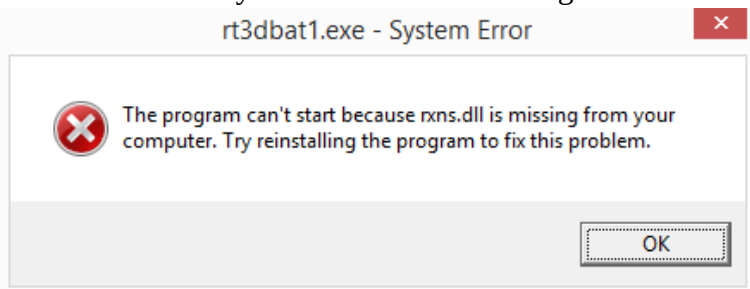


Figure C.1. Error displayed if the user defined dll is not present in the same directory as the rt3dbat1.exe, batch mode utility, when the utility is run.

2. Double click rt3dbat1.exe to run the batch utility.
3. The first question will ask for the total number of components, ncomp, the number of time steps to be used in the batch mode simulation, no_of_timesteps, and the length of each timestep taken, delt. The total time length of the simulation will be number of timesteps, multiplied by the length of each timestep. The user can either enter the values by pressing enter after each value in input, used here, or by separating the values using comma. Answer first question as follows:

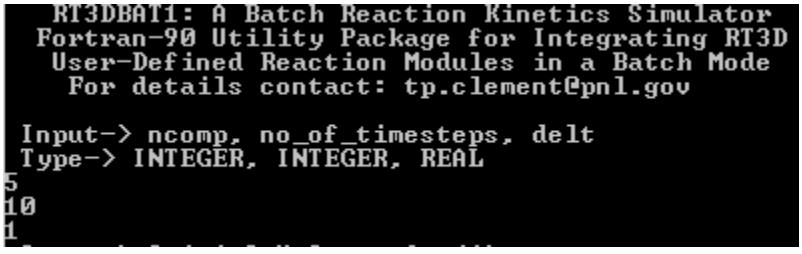


Figure C.2. Figure shows the first question in the batch utility, asking the user to enter the number of components, number of timesteps and the length of each timestep (answers also displayed).

4. The second question will ask for the initial conditions. The values should be entered in the same order as the species listed in Block 5 of the user defined subroutine. Answer the second question as follows:

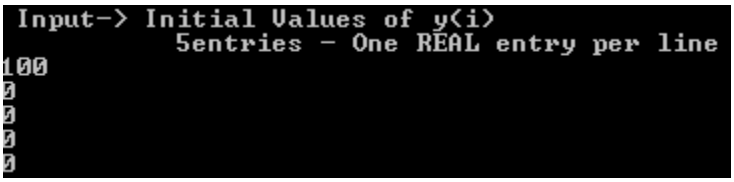


Figure C.3. Figure shows the second question asked by the batch mode utility (answers also displayed). This question asks for the initial conditions.

5. The third question will ask for the tolerances to be used in solving the problem in batch mode, choose n to keep the default values. If need be, the user can test out different tolerance values in order to achieve a reasonable solution; these tolerance values can then also be used in full model run. Answer the third question as follows:

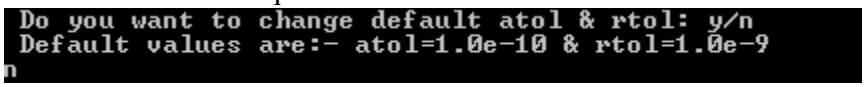


Figure C.4. Figure shows the third question, which asks for tolerance values to be used in batch mode simulation (answer also displayed).

6. The fourth question will ask for the total number of reactions rate constants used in the user defined subroutine. Answer the fourth question as follows:

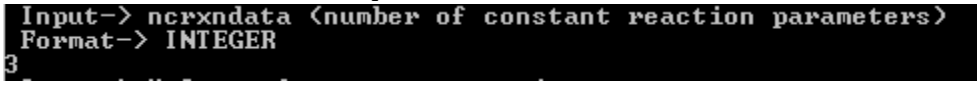


Figure C.5. Figure shows the fourth question which asks for the number of rate constants used (answer also displayed).

7. The fifth question will ask for the user to enter the values for each of the rate constants. The values should be entered in the same order as the rate constants are defined in Block 5 of the user defined script. Answer the fifth question as follows:

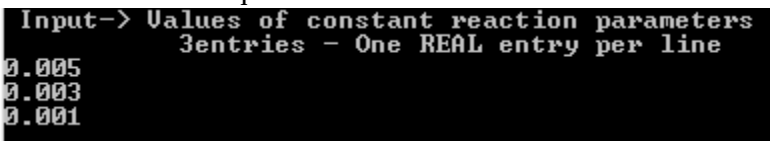


Figure C.6. Figure shows the answer to the fifth question which asks for the values of the rate constants used.

8. Press enter after answering the questions.
9. A file named batchrxn.out will appear in the directory from which the batch utility is run. This file contains the concentration values from the batch mode simulation. The first column will be the time, followed by the concentration values for the species as defined in Block 5 of the user defined subroutine. In this case column 1 is time, column 2 is the concentration of TCE, column 3 is the concentration of DCE, column 4 is the concentration of VC, column 5 is the concentration of ethene and lastly column 6 is the concentration of lactate; results are

below. The user will have to import this .out file into their chosen software to create concentration plots.

0.00000E+00	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.10000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.20000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.30000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.40000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.50000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.60000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.70000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.80000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.90000E+01	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
0.10000E+02	0.10000E+03	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00

Figure C.7. Figure shows the results from the batch mode simulation for scenario 1 in Chapter 2. The results are contained in batchrxn.out file.